ЖУРНАЛ
АНАЛИТИЧЕСКОЙ
ХИМИИ

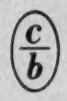
*Volume 14 No. 1*

*January-February 1959*

# JOURNAL OF
# ANALYTICAL CHEMISTRY
## OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMII)

**IN ENGLISH TRANSLATION**



*CONSULTANTS BUREAU*

*Volume 14 No. 1*

*January-February 1959*

# JOURNAL OF
# ANALYTICAL CHEMISTRY
## OF THE USSR

**(ZHURNAL ANALITICHESKOI KHIMII)**

*A publication of the Academy of Sciences of the USSR*

**IN ENGLISH TRANSLATION**

*Year and issue of first translation:*
*Vol. 7, No. 1 Jan.-Feb. 1952*

| | |
|---|---|
| ***Annual subscription*** | ***$80.00*** |
| ***Single issue*** | ***20.00*** |

Copyright 1959
CONSULTANTS BUREAU, INC.
227 W. 17th St., New York 11, N. Y.

Editorial Board
(ZHURNAL ANALITICHESKOI KHIMII)

A.P. Vinogradov (Editor in Chief), I.P. Alimarin, A.M. Dymov, A.P. Terent'ev, D.I. Ryabchikov (Secretary), L.V. Tananaev (Acting Editor), Z.F. Shakhova

---

*A complete copy of any paper in this issue may be purchased from the publisher for $7.50*

*Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners.*

*Printed in the United States of America*

JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume 14, Number 1 January-February 1959

# CONTENTS


| | PAGE | RUSS. PAGE |
|---|---|---|
| Analytical Chemistry in the Forthcoming Seven Years | 1 | 4 |
| Color Reactions of Uranium and Thorium with o'-Arsono-o'-hydroxy-azo-compounds. V. I. Kuznetsov | 5 | 7 |
| Some Characteristics of Selenoyl-2-acetone and Benzoylacetone. A. P. Zozulya, N. N. Mezentseva, V. M. Peshkova, and Yu. K. Yur'ev | 15 | 17 |
| The Use of a Rotating Platinum Micro-Disc Electrode in Polarographic Analysis. M. B. Bardin, Yu. S. Lyalikov, and V. S. Temyanko | 23 | 24 |
| A Study of the Analytical Chemistry of Thallium. Communication 2. Precipitation Reactions of the Bromide Complexes of Trivalent Thallium with Certain Pyrazolone Derivatives. A. I. Busev and V. G. Tiptsova | 27 | 28 |
| The Polarographic Determination of Indium. A. T. Nizhnik and I. S. Chaus | 37 | 37 |
| Increasing the Sensitivity and Accuracy of the Determination of Cesium in Minerals by the Flame-Photometric Method. E. A. Fabrikova | 41 | 41 |
| Spectrochemical Determination of Magnesium and the Effect of the Magnesium Content on the Analysis of Silicon and Manganese in Cast Iron. A. S. Dem'yanchuk and E. D. Kukharenko | 45 | 45 |
| Photometric Determination of Total Rare Earths in Ores and Rocks. F. V. Zaikovskii and V. S. Bashmakova | 51 | 50 |
| Gravimetric and Photometric Determination of the Thorium Content of Uraninites by Means of Anthranilic Acid. Yu. V. Morachevskii and I. A. Tserkovnitskaya | 57 | 55 |
| Kinetic Methods of Quantitative Analysis. Communication 5. A Kinetic Method for the Determination of Tantalum. K. B. Yatsimirskii, O. M. Drobysheva, and V. I. Rigin | 63 | 60 |
| The Polarographic Properties of Niobium in Phosphoric Acid Solutions. D. I. Kurbatov | 67 | 63 |
| Determination of Niobium in the Presence of Tungsten by Means of Cupferron. A. I. Ponomarev and A. Ya. Sheskov'skaya | 71 | 67 |
| A New Luminescent Method of Microchemical Analysis (Crystallophosphor). Communication 1. Detection of Antimony. K. P. Stolyarov and N. I. Grigor'ev | 75 | 71 |
| Determination of Small Amounts of Lead in Rocks. Z. A. Baskova | 81 | 75 |
| Amperometric Titration of Iridium Using a Rotating Platinum Electrode. N. K. Pshenitsyn and N. A. Ezerskaya | 87 | 81 |
| Potentiometric Determination of Phosphate Ions. Z. I. Ivanova and P. N. Kovalenko | 93 | 87 |

# CONTENTS (continued)


| | PAGE | RUSS. PAGE |
|---|---|---|
| Determination of Elemental Sulfur by Extraction with Carbon Tetrachloride. V. P. Gladyshev | 97 | 91 |
| Chemicospectrographic Analysis of Metallic Beryllium and Beryllium Oxide of High Purity. A. G. Karabash, Sh. I. Peizulaev, R. L. Slyusareva, and V. M. Lipatova | 101 | 94 |
| A Semimicro Method for the Isotopic Analysis of Materials with a Deuterium Content Approximating to 100%. A. I. Shatenshtein and Yu. I. Antonchik | 107 | 100 |
| Determination of Micro Amounts of Xenon by Means of the Mass Spectrometer. E. K. Gerling and Yu. A. Shukolyukov | 111 | 104 |
| Conductometric Analysis of Natural Waters. Communication 2. Determination of Magnesium and Anions. G. B. Pasovskaya | 117 | 108 |
| Elemental Organic Analysis by the "Wet Combustion Method". A. P. Terent'ev and B. M. Luskina | 121 | 112 |
| New Method for the Quantitative Determination of Halogens in Organic Material. Communication 4. P. N. Fedoseev and M. Ia. Sobko | 127 | 118 |
| Rapid Methods of Microelemental Analysis. Communication 16. The Relation Between the Length of the Contact Layer and the Method of Decomposition During the Direct Determination of Oxygen. M. O. Korshun and E. A. Bondarevskaya | 133 | 123 |
| Quantitative Determination of the Three Nitrochlorobenzene Isomers in Their Mixtures By Means of Their Infrared Absorption Spectra. V. A. Pozdyshev and É. S. Levin | 139 | 128 |
| The Use of a "Sounding Arc" for Increasing the Reproducibility of Quantitative Determinations in Spectrographic Analysis. Yu. I. Belyaev and É. E. Vainshtein | 145 | 133 |
| Spectrographic Determination of Bismuth, Cadmium, Tin, Lead and Antimony Present as Impurities in Tantalum. E. I. Zakharov, L. V. Lipis, and K. I. Petrov | 147 | 135 |
| The Mass-Spectrometric Analysis of the Isotopic Composition of Boron. G. A. Semenov and Yu. A. Zonov | 151 | 137 |
| Determination of the Various Forms of Iron in Rocks. Yu. P. Trusov | 155 | 139 |
| A Micro Method for the Determination of Fluorine Monoxide. E. A. Peregud and B. S. Boikina | 157 | 141 |
| Determination of Thallium by High-Frequency Titration with Sodium Tetraphenylboron. A. R. Veis and A. F. Ievin'sh | 159 | 143 |

# ANALYTICAL CHEMISTRY IN THE FORTHCOMING SEVEN YEARS

The plan for the development of the national economy of the USSR during 1959-1965, which has been accepted by the twenty-first session of the party, foresees a powerful increase in all branches of the economy of our country, as a result of which a decisive step forward will be made in creating the material-technical basis of communism. The plan has in view the rapid development of a number of the most important branches of the national economy, which will require the participation of analytical chemistry in organizing production control, preparing raw materials, and analyzing finished products. In this connection, analytical chemistry like all Soviet science is confronted by a number of serious, and, to a considerable extent, completely new problems.

The seven-year plan, and also the decisions reached by the May plenum of the Central Committee of the Communist Party of the Soviet Union in 1958, have in view, vast measures to be taken in order to speed up the development of chemical industry, particularly the production of synthetic and natural fibers, plastics, and other synthetics. The forthcoming years will see the "chemicalization" of the country. The total volume of production of the chemical industry will increase almost three times, while that of plastics and synthetic resins will increase 6-7 times. An important feature is that the polymer industry will develop on a new raw-material basis--natural gases and gases obtained as by-products of the petroleum industry. A number of the old branches of the chemical industry such as the production of nitrogeneous fertilizers, will also be based on the use of natural gas. There will be a considerable expansion in the chemical refining of petroleum.

The basic requirement, arising from these changes, which will confront analytical chemists will be to ensure the control of the production of polymeric and other synthetic materials. In this connection the question of considerably extending the work on functional chemical analysis arises. Attention must be focussed in particular on improving methods of analyzing mixtures of hydrocarbons. The ever increasing part played by, and the increase in production of elemental-organic compounds containing silicon, phosphorus, fluorine, and the other elements demand that new methods of analysis by developed for these compounds; work along these lines should, presumably, be concentrated in the same fields as synthetic investigations. The significant increase in attention which should be payed to the analysis of organic compounds is also connected with the necessity of finding methods for the determination of antibiotics and other biological materials. It should be ensured that wide use be made of physical and physicochemical methods of analysis for controlling the production of polymers.

Another important problem arising from the seven-year plan is the problem of the rare elements. The forthcoming years will be characterized by a sharp increase in the production of a number of rare elements, and by an increase in the sphere of their application. Analytical chemistry is confronted by the problem of giving more help to the industry of rare metals, and this help should not be limited only to organizing production control, although this will still remain the chief problem; analytical chemistry should participate in resolving problems connected with complex utilization of raw material, with the search for new sources of rare and scattered elements and intermediates, and studying waste products of various types, etc. The most advanced analytical schemes of separation may become the basis of new technological schemes.

It is essential that during the planning of new enterprises, more attention should be given to questions of production control, it being borne in mind that in a number of cases, the volume of work on control during the actual process may be cut down considerably as a result of organizing rational measures on conditioning the raw material. This is equally true for other branches of industry as well.

The problem which is always connected with the successes of a socialist economy and with the progress of technics, is the problem of determining trace impurities in various materials. This problem is of principal

importance for the development of analytical chemistry as a science since it demands a new approach to analysis, and the development of original methods and equipment for analysis. One of the main fields of application in this connection will be the determination of impurities (down to $10^{-6}$–$10^{-8}$%) in semiconductors, catalysts, and super-pure constructional materials; and determination of "micro elements" playing an important part in biochemical processes. Classical chemical methods which are not suitable for these purposes, will give way more and more to physicochemical and physical methods. Activation analysis, mass spectroscopy, and other modern methods will occupy an important place. The use of radioactive indicators which has been increasing in geometrical progression during recent years for the solution of analytical problems, will, in the forthcoming seven year, undoubtedly become even more important.

The wide and complex mechanization and automation of production processes envisaged by the seven-year plan, is of importance for analytical chemistry in the connection that there will be demands for a considerable increase in the development of chemical principles for automatic control and regulation of production. This is particularly important for the basic chemical, petroleum-refining, and gas industries. Of fundamental importance here will be the reasoned selection of properties and parameters suitable for automatic recording (light absorption, electrical conductivity, etc.), and the development of the appropriate apparatus (meters recorders). The use of instrumental physical and physicochemical methods should serve as a basis for automatic control.

Attention to the needs of ferrous and nonferrous metallurgy, the chemical industry, the mining industry, etc., and also of various branches of science will require further improvement of the classical methods of chemical analysis, and of chromatographic and extraction methods, coprecipitation, etc., which have come into wide use in recent years. From the practical point of view, work on speeding-up analysis and simplifying it is necessary in this connection. It must be emphasized that the problem of the speed of an analysis is a general one, important not only for factory control, but, also for example, for research with short-life radioisotopes.

The solution of all these problems which will arise as a result of the powerful technical progress foreseen by the seven-year plan, is impossible without a fundamental development of the technical basis of analytical chemistry. Naturally, the progress of analytical chemistry as a science is determined by two factors—on the one hand by the demands of life, and practice, and on the other hand by the internal laws of the development of universal analytical chemistry. In evaluating the basis scientific problems confronting analytical chemistry, it is necessary to take both factors into account.

Without doubt an important link in the development of the theoretical aspects is the study of reaction kinetics and mechanisms of analytical importance; here belong oxidation—reduction reactions, complex-formation, and hydrolysis, formation of precipitates, etc. In connection with the wide use of radiochemical methods in analytical chemistry, investigation of the behavior of ultra-small concentrations of materials in solution is becoming increasingly necessary. Of interest is the wider study of the properties of ions (energetic characteristics, etc), since these properties play, in essence, the decisive role in developing analytical methods for one element or another.

Development of the theoretical principles of chromatographic separation, and of coprecipitation, and of the theory of extraction separation of elements and compounds, is one of the real problems of science. There is a need for the development on a wider scale of the theoretical principles of the action of organic reagents for inorganic and organic analysis. The general tendency should be towards an increase in the quantitative sides of research, in particular towards the wider use of the methods of mathematical treatment of experimental results.

Of particular importance is a group of physicochemical and physical methods of analysis comprising, in particular, flame photometry, gas chromatography, oscillographic polarography, and also, hitherto not widely used methods such as electronic and nuclear magnetic resonance. More attention should be given to developing the principles of phase analysis, in which geochemistry, metal treatment, and other sciences are interested; in this connection it is desirable to use physical methods such as radiography.

It is intended during the next seven years to compile new monographs on methods of analysis and the analytical chemistry of individual elements.

One of the most important problems is to improve the organization of scientific-research work, in particular to establish a more rational distribution of the large centers of analytical chemistry. It is necessary to set up a center beyond the Urals so as to ensure that the ever-increasing contigent of analytical chemists in Siberia and the Far East have access to scientific consultation. Coordination of scientific-research work, which should be improved, should be realized not only by convening conferences, but also of scientific conferences, and, to a significant extent, by the active participation of journals on analytical chemistry.

The solution of the new problems set before our analytical chemistry by life, and also the general reorganization of the system of national education in the country, demand improvements in the calibre of analytical chemists. Of fundamental importance in this connection is the acquisition of more profound theoretical knowledge, in the first instance of a physicochemical nature, as well as practical mastery of the most modern, methods of analysis, particularly instrumental methods.

# COLOR REACTIONS OF URANIUM AND THORIUM WITH o'-ARSONO-o'-HYDROXY-AZO-COMPOUNDS*

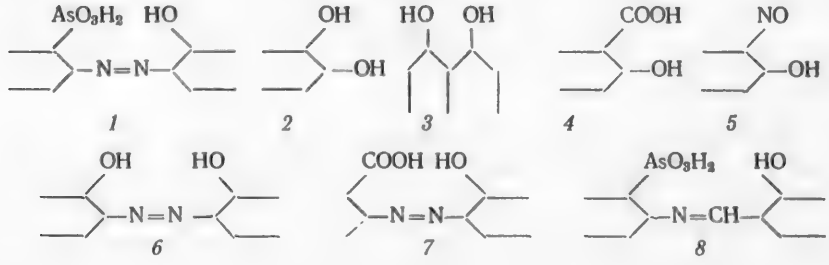
V. I. Kuznetsov

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR

It has been found previously that some compounds containing the atomic group 1 are valuable analytical reagents for the photometric determination of Th, U, total rare earths, Zr, Be and some other elements [1-2]. At present, two reagents found more than 15 years ago, namely thoron and arsenazo (uranon), are finding wide application. They have been recommended for the photometric determination and detection by color reactions of thorium [2-18], uranium [19], the rare earths [20], zirconium [21-22], beryllium [23-25], vanadium [26], lithium [27-29], aluminum [30], and other elements. Thoron is issued as a reagent by foreign firms [31]. Arsenazo—under the name "neotron" — has been recommended by Japanese research workers [32]** for the determination of thorium.

The value of the reagents arsenazo and thoron led the author to study the closest analogs of these reagents. The present article is devoted to some results on the analytical reagents of some of these analogs. The work was carried out in 1942. Some of these analogs, particularly those containing two of these groups in the same molecule,*** proved to be more valuable reagents than arsenazo and thoron.

In accordance with general rules [36, 37] uranium and thorium can give color reactions with many azo-, azomethine, and other colored compounds containing the following atomic groups:

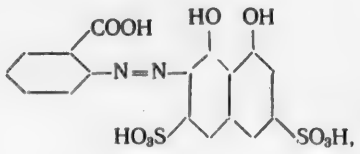



*A paper read on the 12th of March 1957 at a session of the Science Council of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry Acad. Sci. USSR; the paper was devoted to the memory of V. I. Vernadskii.

**The Japanese authors' paper contains no reference to the article of the present author. Presumably, the work of the author [1, 2] was not known to them, although references to this work had been published in Chem. Abstracts and Chem. Zentralblatt, and had been dealt with in detail in F. Welcher's textbook "Organic Analytical Reagents," Vol. IV, pp. 474-75.

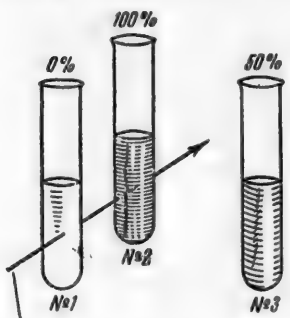
***There have been published references in recent years to the fact that duplication of the same characteristic atomic group in the reagent molecule leads to reagents which give more stable complexes than reagents containing only one such group. Many examples can be quoted to confirm this assertion. This fact is particularly clearly shown in the case of the analogs of 8-hydroxyquinoline [33] and various azo-compounds [34].

of which 2, 3, 4, and 5 may enter into the composition of azo-compounds, di-, and triphenylmethane dyes, hydroxyanthraquinone or indophenols. Of the large number of such possible reagents, those containing group 1 are particularly interesting from the point of view of selectivity, stability of their complexes, and some other characteristics. The reagent arsenazo which contains group 1, forms complexes with U and Th which are more stable than those formed by these metals with its analog which has the following structure




this contains the carboxyl group COOH and not the group $AsO_3H_2$.

Sensitivity of color reactions and stability of the complexes. In Table 1 are given the formulas and rational names of the compounds tested, while Table 2 gives the colors of their solutions, and the colors which develop in the presence of excess thorium. It is evident that compounds in whose molecule group 1 is duplicated, i.e., containing two of the group 1 moieties, do not differ essentially in all cases in color from compounds containing this group only once. But, this duplication of the same group within the molecule essentially increases the stability of the complexes formed by the compound. This means that the complexes of these reagents can be formed under less favorable conditions: at higher acidities, or in the presence of large amounts of phosphates, sulfates, fluorides, and other masking agents. For these reasons reagents with a duplicated group are more valuable than their "monomeric" analogs. Of particular interest are the reagents "thoron II" (VII) and "arsenazo II" (VIII). Examples which illustrate the effect of this duplication of group 1 in the reagent molecule on the stability of the complexes, and the reaction sensitivity connected with this, are given in Table 3. The high sensitivity of the reaction in weakly-acid media with the azo derivatives of chromotropic acid (arsenazo, arsenazo II, X) as compared with that of the corresponding azo derivatives of R-acid (thoron, thoron II, IX) can be explained by the greater contrast of the color changes. But, on the other hand, substituted chromotropic acids are more sensitive with respect to enhanced acidity.




Shade characteristic of binding to the extent of 50%.

Preparing a shade corresponding to binding of the reagent as a complex to the extent of 50%.

In order to make an objective comparison of the stability of the complexes of uranium and thorium formed by the compounds being tested, a new technique was used. We shall give a brief description of this technique.*

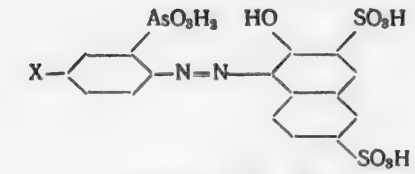
At the test pH, the necessary concentration of the element is chosen so that further increases in this concentration will not lead to a change in the color of the reagent. In this system the reagent is almost completely complexed ("100% color shade"). When this color shade is observed in conjunction with the color of the same concentration of the pure reagent ("0% color shade"), a color shade will be observed which will correspond to the case where the reagent has reacted to the extent of 50% (see Fig. No. 1 and No. 2). It is not difficult to obtain the 50% shade even in one solution, by selecting the concentration of element needed for this, and then taking, for convenience in comparison, double the concentration of the reagent (see Fig. No. 3).

At a constant pH and constant reagent concentration, a definite concentration of free ions of the element corresponds to each color shade. When, for example, an additional amount of element is added to a system with a 50% color shade, and, at the same time, an amount of a chosen masking agent for complexing the element is added so that the shade still remains 50%, then at constant volume, under these conditions, the additional amount of element will be completely masked. This follows from the fact that the equilibrium concentration of the free ions of the element for the system element—reagent and element—masking material is the same, while the equilibrium concentration of free ions of the element required is already created in the

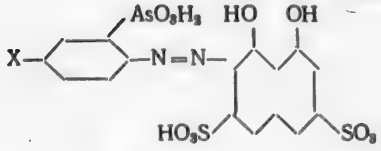
*This technique will be described in detail in subsequent articles.

TABLE 1

Formulas of the Compounds Tested

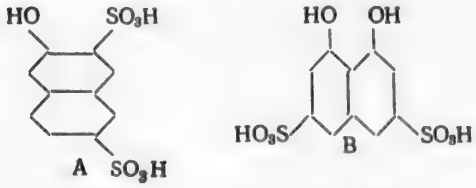


X = H — I (thoron)
$O_2N$ — II (nitrothoron)
$NH_2$ — III (aminothoron)



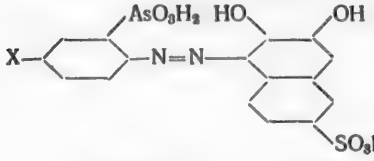
H — IV (arsenazo)
$O_2N$ — V (nitroarsenazo)
$H_2N$ — VI (aminoarsenazo)

R = A VII (thoron II)

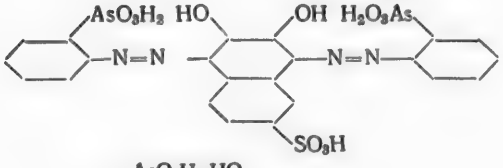


B VIII (arsenazo II)

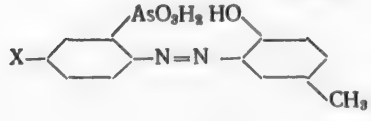
R = A IX
B X



X = H — XI
$O_2N$ — XII
$H_2N$ — XIII



XIV



X = H — XV
$O_2N$ — XVI
$H_2N$ — X VII

I. Benzene-2-arsonic acid-<1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid.

II. 4-Nitrobenzene-2-arsonic acid-<1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid.

III. 4-Aminobenzene-2-arsonic acid-<1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid.

IV. Benzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid.

V. 4-Nitrobenzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid.

VI. 4-Aminobenzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6disulfonic acid.

VII. Diphenyl-4,4'-diarsonic acid-3,3'-bis [<-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid].

VIII. Diphenyl-4,4'-diarsonic acid-3,3'-bis [<-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid].

IX. Diphenyl-3,3'-diarsonic acid-4,4'-bis [<-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid].

X. Diphenyl-3,3'-diarsonic acid-4,4'-bis [<-azo-7>-1,8-dihydroxynaphthalene -3,6-disulfonic acid].

XI. Benzene-2-arsonic acid-<-azo-1>-2,3-dihydroxynaphthalene-6-sulfonic acid.

XII. 4-Nitrobenzene-2-arsonic acid-<1-azo-1>-2,3-dihydroxynaphthalene-6-sulfonic acid.

XIII. 4-Aminobenzene-2-arsonic acid-<1-azo-1>-2,3-dihydroxynaphthalene-6-sulfonic acid.

XIV. 2,3-Dihydroxynaphthalene-6-sulfonic acid-1,4-bis[<-azo-1 >-benzene-2-arsonic acid].

XV. Benzene-2-arsonic acid-<1-azo-6>-1-hydroxy-4-methyl-benzene.

XVI. 4-Nitrobenzene-2-arsonic acid-<-azo-6>-1-hydroxy-4-methylbenzene.

XVII. 4-Aminobenzene-2-arsonic acid-<-azo-6>-1-hydroxy-4-methylbenzene.

TABLE 2

Color Reactions of Thorium

| Compound | Color in weakly-acid medium | |
|---|---|---|
| | reagent alone | reagent + excess of thorium salt |
| Thoron (I) | Yellow | Red rose |
| Thoron II (VII) | Orange yellow | Dark rose |
| (IX) | Bluish raspberry | Bright blue |
| Arsenazo (IV) | Orange red | Blue violet |
| Arsenazo II (VIII) | Orange red | Violet blue |
| (X) | Red violet | Blue |
| (XI) | Orange yellow | Brownish rose |
| (XIV) | Orange rose | Brown lilac |

TABLE 3

Effect of the Duplication of the Same Characteristic Atomic Group within the Molecule of the Reagent on the Sensitivity of the Color Reactions for Thorium

| Reagent | Limiting dilution of thorium in the medium | | | | |
|---|---|---|---|---|---|
| | acetic | 0,1 *N* HCl | 0,5 *N* HCl | 1 *N* HCl | 2 *N* HCl |
| Thoron | $1:3\cdot10^6$ | $1:1,5\cdot10^6$ | $1:0,2\cdot10^6$ | $1:0,08\cdot10^6$ | $1:0,03\cdot10^6$ |
| Thoron II | $1:3\cdot10^6$ | $1:1,5\cdot10^6$ | $1:1,2\cdot10^6$ | $1:1\cdot10^6$ | $1:0,5\cdot10^6$ |
| IX (at. group dupl.) | $1:5\cdot10^6$ | $1:2\cdot10^6$ | $1:0,3\cdot10^6$ | $1:0,1\cdot10^6$ | $1:0,05\cdot10^6$ |
| Arsenazo | $1:5\cdot10^6$ | $1:0,75\cdot10^6$ | | | |
| Arsenazo II | $1:8\cdot10^6$ | $1:1,5\cdot10^6$ | | | |
| X (at. group dupl.) | $1:6\cdot10^6$ | $1:1,5\cdot10^6$ | | | |

solution on reproducing the 50% shade. The molar ratio of the masking agent introduced to the amount of element added, expressed in moles, characterizes the stability of the complex formed by the element and the test reagent. We shall call this value the "stability index of the complex." By comparing, in this way, the results for various reagents, it is possible to get accurate, fully objective stability characteristics of the complexes formed by these reagents. The higher the stability index, the more stable the complex formed with the element. Table 4 contains stability indices for the complexes of uranium and thorium formed by reagents containing one (thoron, arsenazo), and two (thoron II, arsenazo II) of these atomic groups 1. Table 5 contains similar data for arsenazo and its analog similar in structure; arsenazo, however, contains group 1, while its analog contains group 7.

TABLE 4

Comparative Stability of Complexes Formed by the "Single" and "Double" Reagents*

| Masking complexing agent | Indices of the stability of the complex | | | |
|---|---|---|---|---|
| | arsenazo | arsenazo II | thoron | thoron II |
| Thorium, pH 3 | | | | |
| Phosphates | 200 | 400 | 15 | 1000 |
| Tartrates | 70 | 300 | 100 | 800 |
| Fluorides | 20 | 30 | 7 | ~80 |
| Uranium $U^{VI}$, pH 4.5 | | | | |
| Phosphates | 125 | 250 | ~2 | ~3 |
| Tartrates | 160 | 320 | ~3 | ~50 |
| Fluorides | 110 | 180 | ~10 | ~200 |

*The stability indices were determined by S. B. Savvin (The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR).

TABLE 5

Comparison of the Stability of the Complexes of Arsenazo and Its Carboxy Analog*

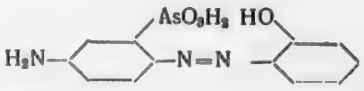
| Masking agent | Stability index of the complex | |
|---|---|---|
| | arsenazo | carboxyl analog |
| Thorium, pH 3.0 | | |
| Phosphates | 200 | 1.4 |
| Tartrates | 70 | 1.6 |
| Fluorides | 20 | 2.8 |
| Uranium $U^{VI}$, pH 4.5 | | |
| Phosphates | 120 | 0.8 |
| Tartrates | 160 | 0.5 |
| Fluorides | 110 | 2 |

*The stability indices were determined by S. B. Savvin (The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR).

### Contrast of the Color Reactions

In Table 6 are given the colors which develop during the reactions with some of the reagents under discussion.

With respect to the contrast of color reactions, reagents containing the amino group, i.e., those containing the following atomic group




are outstanding. Reagents of this type give very contrasting color reactions and deep colors with thorium. Solutions of these reagents themselves differ very little from solutions of their analogs not containing the $NH_2$ group (Table 7).

The reasons for the high contrast of the color reactions of reagents containing the $NH_2$ group, has been discussed in general terms previously [37]. Here, as the result of the formation of a complex in the reagent molecule, there arises a strongly pronounced dipole. An "electric contrast" — in Witsinger's [38] terminology—develops between the different ends of the molecule of the complex, and this circumstance leads to a sharp change in color of the reagent when it is converted into the complex.

In order to illustrate this influence on the color, we may mention an example given in the article on the chromophoric action of the elements [39]. Diazotized amino-hydroxy-azo compounds containing these groups in different nuclei, in the ortho or in the para positions to the azo group, for example

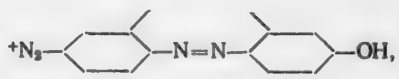


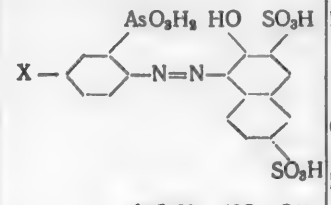
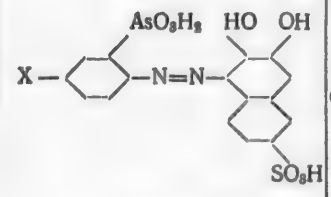
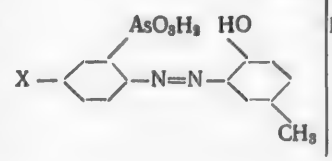
TABLE 6

Color Reactions of Certain Elements at pH 2-4, Except for $U^{VI}$ and Rare-Earths (pH 5-6)

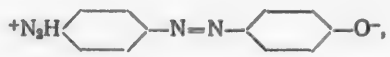
| Reagent | Color | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | reagent alone | Th and $U^{IV}$ | $U^{VI}$ | total rare earths | Ti | Zr | $Sn^{IV}$, β-compound | $Sb^{III}$ | $Nb^{V}$ | $Fe^{III}$ |
| Thoron | Yellow | Rose | Red | Red | Orange | Red-orange | Orange | Orange-red | Orange | Brown |
| Thoron II | Orange-red | Rose | Rose | Rose | Red-orange | Red-orange | Orange | Orange-red | Red-orange | Brown-red |
| IX | Rose | Blue | Blue | Blue-violet | Rose | Rose | Rose | Pale violet | Rose | Brown-red |
| Arsenazo | Orange-red | Blue-violet | Blue | Violet | Violet | Violet | Orange-red | Orange-red | Violet | Brown-violet |
| Nitrothoron | Yellow-orange | Rose | Red | Red | Orange | Orange | Orange | Pale rose | Yellow orange | Brown |
| Amino-thoron | Brown-rose | Blue-violet | Brown-violet | Red-violet | Brown-red | Brown-rose | Brown-yellow | Rose-brown | Brown | Brown-yellow |
| IX | Orange-yellow | Red | Red | Red | Red | Red | Orange | Rose | Rose | Brown-violet |

TABLE 7

Effect of the $H_2N$ Group in Reagent Molecules on the Contrast of Color Reactions with Thorium

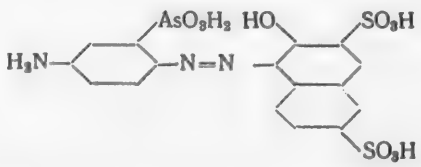
| № | | X | Color | |
|---|---|---|---|---|
| | | | reagent alone | reagent + Th |
| III |  | $H_2N$— | Brownish-rose | Blue-violet |
| I | | H— | Yellow | Rose |
| II | | $O_2N$— | Yellow-orange | Red-rose |
| XIII | | $H_2N$— | Orange-yellow | Red-violet |
| XI |  | H— | Orange-yellow | Red |
| XII | | $O_2N$— | Orange-yellow | Orange-red |
| | | | | Greenish-yellow |
| XVII |  | $H_2N$— | Yellow | Yellow |
| XV | | H— | Yellow | Yellow |
| XVI | | $O_2N$— | Yellow | |

possess a yellow color in acid or in strongly alkaline media (NaOH), while in weakly alkaline media (ammonia, sodium carbonate) they have an exceptionally intense blue color. In this case, in the acid medium or in the strongly alkaline medium there is no strongly developed "electric contrast", since the OH group is not ionized in acid media, while in strongly alkaline media the diazonium cation disappears. In weakly alkaline media, however, the ionic state of the OH group and the diazonium cation



coexist and this fact leads to the intense blue color observed.

In the case of the reagent aminothoron



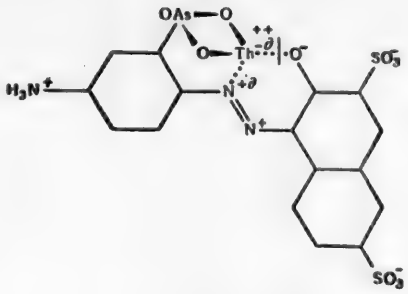
we have a molecule in which both the $NH_2$ and OH groups are in an ionic state, and we get the intense color associated with this state, whatever the pH. In the cyclic salts formed by aminothoron, as a result of intermolecular dissociation of these salts [36] the oxygen of the phenolic group may be in an ionic state even in acid media. When the acidity is sufficient for the $NH_2$ group to change into a salt, then this group also will be in an ionic state. Since thorium forms a complex with aminothoron in strongly acid media, while the rare earths, particularly La, form complexes in very weak acid where the $NH_2$ hardly changes at all into the ionic state, it is readily understood why a more intense color is given with thorium than with lanthanum.

Aminothoron gives the following colors:

| | | |
|---|---|---|
| Reagent alone | pH 3—6 | Brownish-rose |
| Thorium | 3.0 | Blue-violet |
| Uranium (VI) | 4.2 | Brownish-violet |
| Lanthanum | 6.0 | Brownish-raspberry |

Aminothoron only forms brownish-rose and brownish-reddish colors with zirconium and titanium, respectively. It would be thought that with these elements, as with thorium, there should develop intense violet colors, since the reactions take place in a strongly acid medium. This, however, is not the case because zirconium and titanium only weakly favor the change over into the ionic state of the nitrogen of the amino group, which also deepens the color. The same phenomenon is observed in the case of reagent thoron: with thorium a rose color develops, while with zirconium and titanium only an orange-red color develops.

Taking into account chemical considerations and the color observed, the following structure can be assigned to the violet stage of the complex of thorium with the reagent aminothoron



Synthesis of the compounds tested. Synthesis of most of the azo compounds tested, many of which have not hitherto been described in the literature, did not lead to any difficulties and was carried out by the usual azo coupling method. Almost all of them in the form of the free acids or their salts can be readily crystallized, so that their purification is straightforward. The compounds used as the diazotized component were the following compounds which have been described in the literature: 2-aminophenyl-arsonic acid [40], 3,3'-diaminodiphenyl-4,4'-diarsonic acid [41], and 5-nitro-2-aminophenylarsonic acid [42].

Compounds containing the $NH_2$ group were obtained from the corresponding nitro compounds by reduction of the latter by gentle heating with sodium sulfide in an alkaline medium, followed by precipitation of excess sulfide with copper salts (in the presence of NaOH), and separation of the end-product by acidification or salting out (aminothoron).

2,3-Dihydroxynaphthalene-6-sulfonic acid was used as the azo component for the compounds XI, XII, and XIV. The position of the sulfonate group in XI, XII, and XIII has not been established; it is possible that it occupies position 7, not 6.

Benzidene-3,3'-diarsonic acid, which apparently has not yet been described in the literature, was used for synthesizing IX and X. We did not isolate it in a pure form. The reaction product obtained from o-nitrophenyl arsonic acid was used directly without purification for diazotization and coupling; it was prepared in a similar manner to that used for the preparation benzidene-3,3'-dicarboxylic acid by reduction to the hydrazo compound, by the action of zinc dust and NaOH, with subsequent regrouping in the presence of concentrated hydrochloric acid. In view of the ease with which it could be oxidized, the pale-yellowish alkaline solution of the hydrazo compound was filtered from the zinc sludge directly into cold concentrated hydrochloric acid. The monoazo compound (reduction of o-nitrophenylarsonic acid to o-aminophenylarsonic acid) predominated in the products obtained by azo coupling.

Diazo compounds IX and X were separated and purified chromatographically on $Al_2O_3$. Dilute 0.5-1% acetic acid completely elutes the monoazo compound, while it does not elute the diazo compound. After elution of the monoazo compound, the diazo compound was eluted with a solution of $NaHCO_3$. The yield of final IX and X, calculated on the basis of o-nitrophenylarsonic acid was very small.

## SUMMARY

Colored organic reagents which give color reactions with uranium and thorium may contain various characteristic atomic groups. The most interesting reagents are those which contain group 1; the well-known reagents thoron and arsenazo belong to this category. The color reactions of 15 other compounds containing this characteristic atomic group have been studied.

New reagents, thoron II (diphenyl-4,4'-diarsonic acid-3,3'-bis[<-azo>-2-hydroxynaphthalene-3,6-disulfonic acid]), and arsenazo II (diphenyl-4,4'diarsonic acid-3,3'-bis[<-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid]) in which group 1 is duplicated,are described. The molecules of these new reagents are doubled molecules of thoron and arsenazo, respectively. Arsenazo II and thoron II give more stable complexes than arsenazo and thoron, as a result of which colors develop in more acid solutions and in the presence of larger amounts of sulfates, phosphates, and other masking agents, than when arsenazo and thoron are used. The shade of the colors which are formed by arsenazo II and thoron II differ little from those given by arsenazo and thoron.

With respect to the contrast of its color reaction, the reagent aminothoron (4-aminobenzene-2-arsonic acid-<-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid) is outstanding; it gives a violet color with thorium in acid media. The solutions of aminothoron itself are yellow brown in color. The reasons for the contrast of the color reactions of aminothoron are discussed.

Schemes for the synthesis of the compounds tested are given; most of them have not hitherto been described in the literature.


## LITERATURE CITED


[1] V. I. Kuznetsov, Proc. Acad. Sci. 31, 895 (1951).

[2] V. I. Kuznetsov, J. Gen. Chem. 14, 914 (1944).

[3] P. E. Thomason, M. A. Perry and W. M. Byerly, Report Mon C-83, Mar. 11, 1946; Analyt. Chem. 21, 1239 (1949).

[4] C. J. Rodden and J. C. Warf, Analyt. Chem. of Manhattan Project, Division VIII, vol. 1, p. 160, New York — Toronto — London, McGraw, 1950; in C. A. 45, 7466 (1951).

[5] J. C. Ingles, Canad. Chem. a proc. Ind. 35, N 5, 397, 400-402, 404, 406.

[6]R. Kronstadt and A. R. Eberle, Atomic Energy Commission Report, RMO — 838, 1952 (quoted in [13]).

[7] A. Mayer and G. Bradshau, Analyst. 77, 154 (1952).

[8]A. E. Taylor and R. T. Dillon, Analyt. Chem. 24, 1624 (1952).

[9] R. J. Geest, Can. Dept. Mines and Tech. Surveys. Tech. Paper N 1, 24 pp. (1953); in C.A. 47, 6305 (1953).

[10] C. H. Byrd, Abstr. doctoral thesis,Chem. Iowa State Coll. 1953-1954, Iowa State Coll. J. Sci. 1955, 29, N 3 , 389; Ref. Chem. J. 1956, 4159 (N 2).

[11] C. V. Banks and C.H. Byrd, Analyt. Chem. 25, 416 (1953).

[12] C. V. Banks, D. W. Klingmann, and C. H. Byrd., Analyt. Chem. 25, 992 (1953).

[13] D. W. Margerum, Analyt. Chem. 25, 1219 (1953).

[14] J. C. Dalton and S. J. Thomson, Geochim. et Cosmochim. Acta 5, 74 (1954).

[15] L. P. Adamovich and V. M. Rutman, Sci. Proc. Kharkov University, 54, 1954, Trans. NIIkhimii*13, 203.

[16] J. Clinch, Analyt. chim. Acta 14, 162 (1956).

[17] F. S. Grimaldi and M. H. Fletcher, Analyt Chem. 28, 812 (1956).


*Scientific Research Institute of Chemistry.

[18] V. L. Kuznetsov, and L. V. Nikol'skaya, J. Anal. Chem. (In the press).*

[19] V. L. Kuznetsov, J. Anal. Chem. 13, 220 (1958).*

[20] V. L. Kuznetsov, J. Anal. Chem. 7, 226 (1952).

[21] A. D. Horton, Analyt Chem. 25, 1331 (1953).

[22] V. L. Kuznetsov, L. M. Budanova, and T. V. Matrosova, Industrial Labs. 22, 406 (1956).

[23] V. L. Kuznetsov, J.Anal.Chem. 10, 276 (1955).

[24] L. P. Adamovich and A. P. Mirnaya, "Modern Methods of Analysis in Metallurgy," Symposium in Russian, Metallurgizdat, Moscow, 1955, p. 172.

[25] L. P. Adamovich and B.V. Yutsis, Ukranian Chem. J. 22, 523 (1956).

[26] V. L. Kuznetsov, Proc. Acad. Sci. 52, 39 (1946).

[27] V. L. Kuznetsov, J. Anal. Chem. 3, 295 (1948).

[28] A. V. Nikolaev and A. A. Sorokina, Proc. Acad. Sci. 77, 427 (1951).

[29] P. F. Thomason, Analyt Chem. 28, 1527 (1956).

[30] V. L. Kuznetsov and R. B. Golubtsova, Industrial Labs. 21, 1422 (1955); 22, 161 (1956).

[31] See, for example, Nature, 169, U 4305, cmp. CCLXXXY (May 3, 1952, Analyt. chim. Acta, 7, N 3 (1952).

[32] M. Ishibashi and S. Higashi, Japan Analyst. 4 (1), 4 (1955); 5 (3), 135 (1956); in Anal. Abstr. 2, 2387 (1955); 3, 3011 (1956).

[33] V. M. Dziomko, see Collection of Articles in All-Union Correspondence Polytech. Inst. 5, 105 (1953).

[34] V. L. Kuznetsov, Trans. Commission on Anal. Chem. VI (IX), 255 (1955).

[35] V. L. Kuznetsov, J. Anal. Chem. 2, 67 (1947).* *

[36] V. L. Kuznetsov, J. Gen. Chem. 20, 807, 816 (1950).*

[37] V. L. Kuznetsov, Proc. Acad. Sci. 50, 233 (1945).

[38] R. Witzinger, "Organic Dyes on the Basis of Coordination Theory", [Translated from German] ONTI, Leningrad, 1936, p. 38.

[39] V. L. Kuznetsov, Prog. Chem. 21, 175 (1952).

[40] D. M. Rozina, J. Appl. Chem. 23, 1110 (1950).*

[41] W. W. Bauer and R. Adams, J. Amer. Chem. Soc. 46, 1927 (1931).

[42] L. Benda, Ber. 44, 3294 (1912).

Received February 20, 1958

*Original Russian pagination. See C.B. Translation.

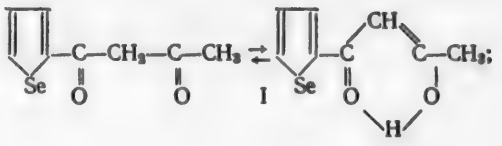
**Not mentioned in Russian text – Publisher's note.

# SOME CHARACTERISTICS OF SELENOYL-2-ACETONE AND BENZOYLACETONE

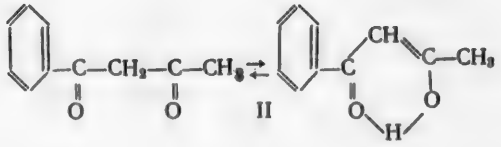
A. P. Zozulya, N. N. Mezentseva, V. M. Peshkova, and Yu. K. Yur'ev

The M. V. Lomonosov Moscow State University

In studying complex formation processes by means of the distribution method (extraction), it is necessary to carry out a preliminary determination of the constants of acid dissociation of the reagents used, and also the partition constants of the undissociated molecules of these reagents in the systems chosen, at different concentrations of reagent in the organic solvent layer [1, 2]. In the work described here, these characteristics were determined for selenoyl-2-acetone which has been synthesized for the first time (I) and benzoylacetone which has been described previously (II).



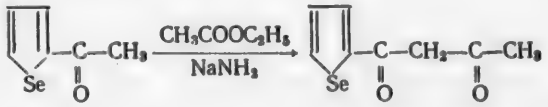
I



II

## EXPERIMENTAL

Reagents used. Selenoyl-2-acetone was synthesized for the first time by N. N. Mezentseva in the laboratory of Yu. K. Yur'ev according to the following scheme:



To sodium amide obtained from 8.6 g of sodium [13] and dissolved in 300 ml of absolute ether contained in a three-necked flask fitted with a stirrer, condenser, and dropping funnel, was added, at 20° with stirring, a solution of 30 g (0.17 g • mole) of methyl-(selenoyl-2)-ketone in 25 ml of absolute ether; this was followed by a solution of 40 g (0.45 g • mole) of absolute ethyl acetate in 40 ml of absolute ether. The reaction mixture was stirred for 15 minutes at 20°, and for 3 hours while heating on a water bath. After cooling, the reaction mass was decomposed with a mixture of ice (about 400 g) and 90 ml of concentrated hydrochloric acid and the resultant mixture extracted with ether. The combined ether extracts were dried with anhydrous

magnesium sulfate. After distilling off the ether, the residue was distilled under vacuum. 26 g of product was obtained (71%); the boiling point was 146-146.5° at 7 mm (a viscous oil with a straw-yellow color which crystallized in the receiver); m.p. 33-33.5° (from alcohol). Analysis in % C 44.81, 44.77; H 3.87, 3.80: Calculated in %: C 44.67; H 3.75. The preparation was carefully purified and stored until its weight was almost constant.

The benzoylacetone which was synthesized [4] was subjected to repeated crystallization from ethanol until white crystals with a m. p. of 58.5-59° were obtained. The absorption spectrum of the reagent thus prepared agreed with that published in the literature [5]. The benzoylacetone was stored in a desiccator until its weight was almost constant. Preparation of the NaOH and $NaClO_4$ solutions used in the course of the work, as well as purification of the solvents used, were the same as described previously [6].

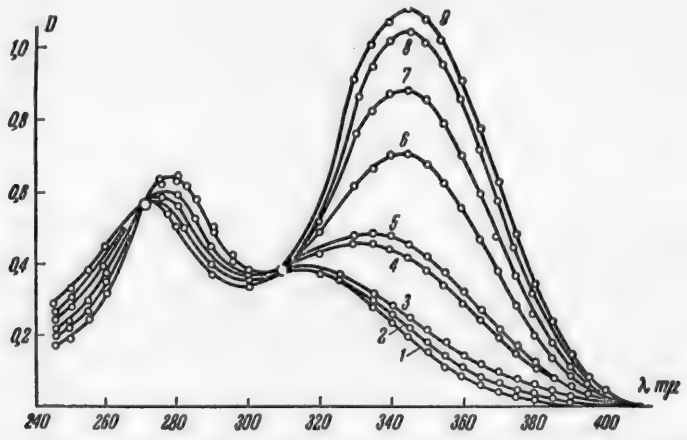



Fig. 1. Absorption curves for aqueous solutions of selenoyl-2-acetone at various pH's: 1) 2.01; 2) 5.32; 3) 7.51; 4) 7.92; 5) 8.20; 6) 8.60; 7) 9.12; 8) 9.90; 9) 11.15.

Experimental procedure. For determination of the acid dissociation constants of the reagents, known equal volumes of an aqueous solution of the test reagent (the reagent solution was prepared by dissolving a small amount of the solid reagent in aqueous $HClO_4$ at a pH of about 1) were introduced into a series of 50 ml flasks; the reagent solutions in the flasks were diluted slightly with water and the calculated amounts of NaOH and 0.5 N $NaClO_4$ added, the volumes were then made up to the mark (ionic strength of the final solution was $\mu = 0.1$). The procedure subsequently followed for determination of the dissociation constants and the partition constants was the same as that described already [6].

Determination of the acid dissociation constant of selenoyl-2-acetone and benzoylacetone was carried out photometrically using the method of "isobestic points" [7], which has been successfully used for studying the reagents themselves [8-10] as well as complexes formed by reagents with metals [11]. On the absorption curves of aqueous solutions of selenoyl-2- and benzoylacetone, having different pH values, there is observed a definite shift in the absorption maximum; this shift is determined by the dissociation of the reagent, and by differences in the absorption of its dissociated and undissociated forms (Figs. 1 and 2).* It was established beforehand that the absorption curves for selenoyl-2-acetone and benzoylacetone solutions having a pH of $< 2.5$ and $\leq 2.1$, respectively, correspond to absorption of the almost completely undissociated forms, while the absorption curves for solutions having pH 10.9 and 10, respectively, correspond to absorption of the almost completely dissociated forms (curves for solutions within the pH range 5-10 correspond to absorption by mixtures of the dissociated and undissociated forms of the reagents). At a constant total concentration of the reagent in aqueous solution, the value of the acid dissociation constant is calculated according to the following equation

$$K_{dissoc.} = \frac{(A_{mixture} - A_{undissoc.})}{(A_{dissoc.} - A_{mixture})} \cdot (H^+), \qquad (1)$$

*In the middle region of Fig. 1, the numeration of the curves is the reverse of that for the right-hand side. Some of the curves coincide with each other between the first and second "isobestic" points.

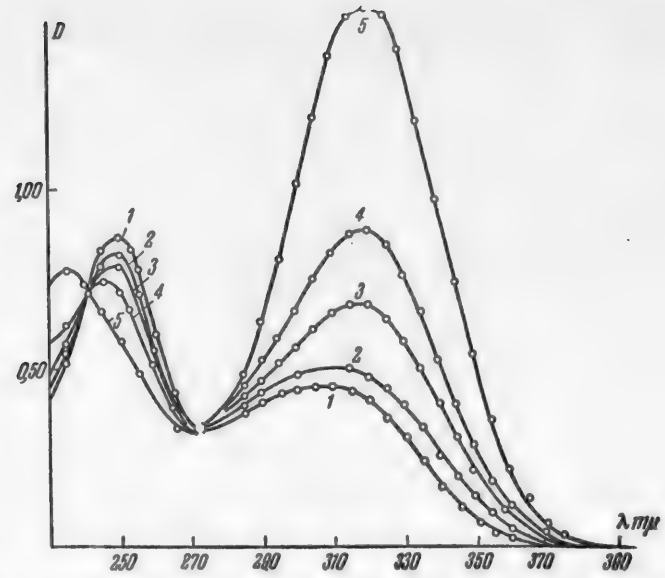



Fig. 2. Absorption curves for aqueous solutions of benzoylacetone at various pH values: 1) 2.06; 2) 7.85; 3) 8.42; 4) 8.90; 5) 10.90.

TABLE 1

Relationship between the Optical Density of Aqueous Solutions of Selenoyl-2-acetone and Hydrogen Ion Concentration

| λ mμ | pH | | | | | |
|---|---|---|---|---|---|---|
| | 2,01 | 7.02 | 8,20 | 8,60 | 9,12 | 11,15 |
| 330 | 0,317 | 0,455 | 0,473 | 0,620 | 0,760 | 0,920 |
| 335 | 0,280 | 0,454 | 0,480 | 0,665 | 0,820 | 1,010 |
| 340 | 0,243 | 0,443 | 0,473 | 0,700 | 0,870 | 1,080 |
| 345 | 0,201 | 0,422 | 0,456 | 0,705 | 0,880 | 1,120 |
| 350 | 0,160 | 0,385 | 0,422 | 0,675 | 0,860 | 1,090 |
| 355 | 0,122 | 0,345 | 0,376 | 0,628 | 0,800 | 1,030 |
| 360 | 0,087 | 0,295 | 0,327 | 0,553 | 0,705 | 0,912 |
| 365 | 0,063 | 0,244 | 0,273 | 0,465 | 0,600 | 0,780 |
| 370 | 0,046 | 0,196 | 0,218 | 0,380 | 0,482 | 0,630 |

Note, Only curves 4, 5, 6, and 7 (Fig. 1) were used for calculation. Curves 2, 3, and 8 were not used since the small difference in optical densities obtained thereby, may lead to appreciable errors in the value of $K_{dissoc.}$.

where $A_{undissoc.}$, $A_{dissoc.}$, and $A_{mixture}$ are the optical densities of solutions containing the undissociated, dissociated, and mixtures of dissociated and undissociated forms of the reagent, respectively, for a given wavelength and ($H^+$) is the hydrogen ion concentration of the solution containing both forms of the reagent. The values of the optical density chosen for calculation are given in Tables 1 and 2 for selenoyl-2-acetone and benzoylacetone, respectively. The calculated values for the reciprocal logarithm of the dissociation constant ($pK_{dissoc.}$) of selenoyl-2-acetone and benzoylacetone are: $pK_{dissoc.} = 8.55 \pm 0.08$ (mean of 36 calculated values) and $pK_{dissoc.} = 8.96 \pm 0.09$ (mean of 27 calculated values), respectively.

TABLE 2

Relationship between the Optical Density of Aqueous Solutions of Benzoylacetone and Hydrogen Ion Concentration

| λ mμ | pH | | | | |
|---|---|---|---|---|---|
| | 2,06 | 7,85 | 8,42 | 8,90 | 10,90 |
| 305 | 0,442 | — | 0,605 | 0,750 | 1,20$_0$ |
| 310 | 0,446 | 0,490 | 0,651 | 0,830 | 1,38$_0$ |
| 315 | 0,436 | 0,510 | 0,678 | 0,880 | 1,50$_0$ |
| 320 | 0,410 | 0,480 | 0,678 | 0,890 | 1,51$_0$ |
| 325 | 0,364 | 0,458 | 0,642 | 0,850 | 1,50$_0$ |
| 330 | 0,306 | 0,406 | 0,585 | 0,770 | 1,40$_0$ |
| 335 | 0,237 | 0,337 | 0,499 | 0,658 | 1,20$_0$ |
| 340 | 0,165 | 0,265 | 0,402 | 0,528 | 0,980 |
| 345 | 0,112 | — | 0,310 | 0,404 | 0,748 |

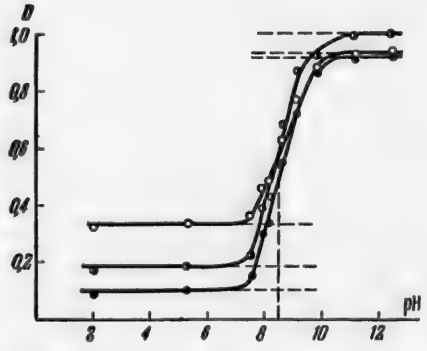



Fig. 3. Relation between the optical density of solutions of selenoyl-2-acetone and the pH at various wave lengths ○) 330 mμ; □) 350 mμ; △) 360 mμ.

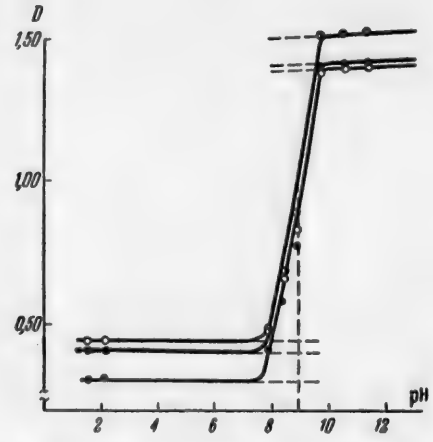



Fig. 4. Relation between the optical density of solutions of benzoylacetone and the pH at various wave lengths ○) 310 mμ; □) 320 mμ; △) 330 mμ.

TABLE 3

Distribution Constant (I) of Selenoyl-2-acetone in the System $CHCl_3$–$H_2O$ ($t = 25 \pm 0.1°$; $\mu = 0.1$)

| Initial concentration in $CHCl_3$, in moles/liter | Amount of (I) found in the aqueous phase in g/15 ml | Amount of (I) found in the $CHCl_3$ phase, in g/15 ml | Log $K_{distrib.}$ | $K_{distrib.}$ |
|---|---|---|---|---|
| $1{,}29 \cdot 10^{-1}$ | $4{,}95 \cdot 10^{-4}$ | $41{,}54 \cdot 10^{-2}$ | 2,924 | 839 |
| $6{,}50 \cdot 10^{-2}$ | $2{,}49 \cdot 10^{-4}$ | $20{,}77 \cdot 10^{-2}$ | 2,921 | 834 |
| $5{,}00 \cdot 10^{-2}$ | $1{,}98 \cdot 10^{-4}$ | $16{,}12 \cdot 10^{-2}$ | 2,911 | 815 |
| $3{,}90 \cdot 10^{-2}$ | $1{,}44 \cdot 10^{-4}$ | $12{,}46 \cdot 10^{-2}$ | 2,937 | 851 |
| $2{,}50 \cdot 10^{-2}$ | $0{,}96 \cdot 10^{-4}$ | $80{,}60 \cdot 10^{-3}$ | 2,924 | 839 |
| $1{,}00 \cdot 10^{-2}$ | $0{,}39 \cdot 10^{-4}$ | $32{,}25 \cdot 10^{-3}$ | 2,917 | 826 |
| $5{,}00 \cdot 10^{-3}$ | $0{,}18 \cdot 10^{-4}$ | $16{,}12 \cdot 10^{-3}$ | 2,952 | 895 |

It is known that the values of $pK_{dissoc.}$ can be determined by a purely graphical method from the curves relating the optical density at a definite wave-length to the pH of aqueous solutions. The perpendicular dropped from the middle part of the steep part of the curves onto the abscissa gives the numerical value of the reciprocal logarithm of the acid dissociation constant of the reagent. The values obtained in this way (Figs. 3 and 4) for the acid dissociations of the reagents studied ($pK_{dissoc.}$ selenoyl-2-acetone $= 8.60 \pm 0.07$ and $pK_{dissoc.}$ benzoylacetone $= 8.90 \pm 0.09$) coincide satisfactorily with the values calculated from the absorption curves.

Determination of the distribution constants of selenoyl-2-acetone and benzoylacetone in systems of chloroform or benzene-water. The distribution constants of the reagent studied ($K_{distrib.}$)* must be determined over a fairly wide concentration range of the reagent in the organic solvent layer.

TABLE 4

Distribution Constant of Selenoyl-2-acetone (I) in the System $C_6H_6$—$H_2O$ ($t = 25 \pm 0.1°$; $\mu = 0.1$)

| Initial concentration of (I) in $C_6H_6$, in mole per liter | Amount of (I) found in the aqueous phase, in g/15 ml | Amount of (I) found in the $C_6H_6$, in g/ml | Log $K_{distrib.}$ | $K_{distrib.}$ |
|---|---|---|---|---|
| $8,74 \cdot 10^{-2}$ | $2,73 \cdot 10^{-4}$ | $28,17 \cdot 10^{-2}$ | 2,998 | 995 |
| $5.83 \cdot 10^{-2}$ | $1,83 \cdot 10^{-4}$ | $18,78 \cdot 10^{-2}$ | 3,011 | 10_6 |
| $4,37 \cdot 10^{-2}$ | $1,38 \cdot 10^{-4}$ | $14,09 \cdot 10^{-2}$ | 3,009 | 1021 |
| $2,91 \cdot 10^{-2}$ | $0,90 \cdot 10^{-4}$ | $93,91 \cdot 10^{-3}$ | 3,012 | 1028 |
| $1,75 \cdot 10^{-2}$ | $0,57 \cdot 10^{-4}$ | $56,34 \cdot 10^{-3}$ | 2,995 | 088 |
| $1,16 \cdot 10^{-2}$ | $0,39 \cdot 10^{-4}$ | $37,56 \cdot 10^{-3}$ | 2,984 | 964 |
| $8,74 \cdot 10^{-3}$ | $0,26 \cdot 10^{-4}$ | $28,17 \cdot 10^{-3}$ | 3,018 | 1042 |

TABLE 5

Distribution Constant of Benzoylacetone (II) in the System $CHCl_3$—$H_2O$ ($t = 25 \pm 0.1°$; $\mu = 0.1$)

| Initial concentration of (II) in $CHCl_3$, in mole per liter | Amount of (II) found in the aqueous phase, in g/15 ml | Amount of (II) found in the $CHCl_3$, phase, in g/15 ml | Log $K_{distrib.}$ | $K_{distrib.}$ |
|---|---|---|---|---|
| $1,50 \cdot 10^{-1}$ | $1,16 \cdot 10^{-4}$ | $36,48 \cdot 10^{-2}$ | 3,462 | 2897 |
| $1,30 \cdot 10^{-1}$ | $1,17 \cdot 10^{-4}$ | $31,61 \cdot 10^{-2}$ | 3,432 | 2704 |
| $1,20 \cdot 10^{-1}$ | $1,02 \cdot 10^{-4}$ | $29,18 \cdot 10^{-2}$ | 3,457 | 2864 |
| $1,00 \cdot 10^{-1}$ | $0,87 \cdot 10^{-4}$ | $24,32 \cdot 10^{-2}$ | 3,447 | 2799 |
| $5,00 \cdot 10^{-2}$ | $0,45 \cdot 10^{-4}$ | $12,16 \cdot 10^{-2}$ | 3,432 | 2704 |
| $3,00 \cdot 10^{-2}$ | $0,27 \cdot 10^{-4}$ | $72,95 \cdot 10^{-3}$ | 3,432 | 2704 |
| $2,00 \cdot 10^{-2}$ | $0,18 \cdot 10^{-4}$ | $48,64,10^{-3}$ | 3,432 | 2704 |
| $1,50 \cdot 10^{-2}$ | $0,15 \cdot 10^{-4}$ | $36,46 \cdot 10^{-3}$ | 3,386 | 2432 |

We studied the distribution of undissociated molecules of selenoyl-2-acetone and benzoylactone in the systems $CHCl_3$—$H_2O$ and $C_6H_6$—$H_2O$ at an ionic strength of the latter of $\mu = 1$, and at a temperature of $25 \pm \pm 0.1°$, for the original concentrations of reagents in the organic solvent indicated in Tables 3, 4, 5, and 6. The values obtained for the distribution constant of selenoyl-2-acetone are given in Tables 3 and 4; while analogous results are given for benzoylacetone in Tables 5 and 6. The nature of the changes in $K_{distrib.}$ in the studied concentration range of the reagents is evident from Figs. 5 and 6 (values for log $K_{distrib.}$ ** are given.

*$K_{distrib.} = \frac{C_{org.}}{C_{water}}$, where $C_{org}$ and $C_{water}$ are the equilibrium concentrations of the reagent in the organic and aqueous-phases, respectively.

**Each value for $K_{distrib.}$ given in Tables 3-6 is the mean of two-three replicate determinations.

TABLE 6

Distribution Constant of Benzoylacetone (II) in the System $C_6H_6 - H_{20}$ ($t = 25 \pm 0.1°$; $\mu = 0.1$)

| Initial concentration of (II) in $C_6H_6$, in mole per liter | Amount of (II) found in the aqueous phase, in g/15 ml | Amount of (II) found in the $C_6H_6$ phase, in g/15 ml | Log $K_{distrib.}$ | $K_{distrib.}$ |
|---|---|---|---|---|
| $1,50 \cdot 10^{-1}$ | $2,64 \cdot 10^{-4}$ | $36,45 \cdot 10^{-2}$ | 3,140 | 1380 |
| $1,30 \cdot 10^{-1}$ | $2,28 \cdot 10^{-4}$ | $31,60 \cdot 10^{-2}$ | 3,142 | 1387 |
| $1,20 \cdot 10^{-1}$ | $2,04 \cdot 10^{-4}$ | $29,17 \cdot 10^{-2}$ | 3,155 | 1429 |
| $1,00 \cdot 10^{-1}$ | $1,71 \cdot 10^{-4}$ | $24,31 \cdot 10^{-2}$ | 3,153 | 1422 |
| $5,00 \cdot 10^{-2}$ | $0,87 \cdot 10^{-4}$ | $12,15 \cdot 10^{-2}$ | 3,145 | 1396 |
| $3,00 \cdot 10^{-2}$ | $0,54 \cdot 10^{-4}$ | $72,90 \cdot 10^{-3}$ | 3,130 | 1349 |
| $2,00 \cdot 10^{-2}$ | $0,33 \cdot 10^{-4}$ | $48,62 \cdot 10^{-3}$ | 3,168 | 1472 |
| $1,50 \cdot 10^{-2}$ | $0,27 \cdot 10^{-4}$ | $36,45 \cdot 10^{-3}$ | 3,130 | 1349 |

For calculating the mean value of $K_{distrib.}$ (Tables 3-6), results which did not differ from each other by more than 6% were used. The values found for the distribution constant of selenoyl-2-acetone were as follows: 1) for the system $CHCl_3 - H_{20}$, $K_{distrib.} = 839 \pm 9$ ($\log K_{distrib.} = 2.922 \pm 0.006$); 2) for the system $C_6H_6$, $K_{distrib.} = 1009 \pm 23$ ($\log K_{distrib.} = 3.004 \pm 0.010$).

The values found for the distribution constant of benzoylacetone were as follows: 1) for the system $CHCl_3 - H_2O$, $K_{distrib.} = 2746 \pm 60$ ($\log K_{distrib.} = 3.439 \pm 0.009$); 2) for the system $C_6H_6 - H_2O$, $K_{distrib.} = 1398 \pm 32$ ($\log K_{distrib.} = 3.145 \pm 0.010$).

## DISCUSSION OF RESULTS

The fact that there are two fairly clearly defined isobestic points on the absorption curves for aqueous solutions of both selenoyl-2-acetone and benzoyl acetone, indicates the presence of two absorption centers in the solution. The predominance of one of the forms of the reagent, under certain conditions, is confirmed by the almost complete coincidence of the absorption curves obtained for groups of solutions having a pH less than 2 and greater than 10, and also by the fact that the absorption exhibited by the solutions conforms to the Beer Law at various wave lengths. (this fact was verified for the group of solutions with pH > 10).

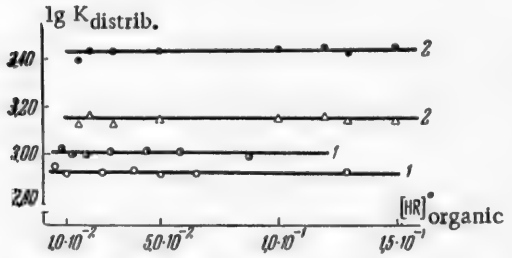



Fig. 5. Relation between the distribution constant of selenoyl-2-acetone (I) and benzoylacetone (II), and the concentration of reagent in the organic solvent (1— O— $CHCl_3$—aqueous phase; ⊙—$C_6H_6$ — aqueous phase; 2) — □— $CHCl_3$ — aqueous phase; Δ— $C_6H_6$ —aqueous phase).

The acid dissociation constant of selenoyl-2-acetone determined at an ionic strength of 0.1, and the value obtained, do not contradict conclusions which can be drawn from a comparison of the dissociation constants of analogs of acetylacetone. The dissociation constant of benzoylacetone has been determined polarographically previously by Tachi [12], and also by Eidinoff [13] who measured the pH of partially neutralized solutions of the reagent in aqueous-alcoholic media, containing up 7.4% of ethanol. The value obtained by Tachi ($K_{dissoc.} = 3.2 \times 10^{-7}$) would appear to be high; this might be the result of small amounts of impurities in the test solution. The value found by Eidinoff for the dissociation constant ($pK_{dissoc.} = 8.697 \pm 0.005$) is fairly close to the value we obtained. Some of the deviation in the results may be caused by differences in the conditions used for determining the characteristics studied (different ionic strength of the solution, the presence of an appreciable amount of alcohol, etc.). The value which we found for the dissociation constant of benzoylacetone, namely, $pK_{dissoc.} = 8.96 \pm 0.09$ does not disagree with the values obtained for the same characteristic for acetylacetone ($pK_{dissoc.} = 8.82$ [14], $pK_{dissoc.} = 8.93$ [13] et al), which is an analog of benzoylacetone. The similarity in

the structure of selenoyl-2-acetone and acetylacetone explains the comparatively insignificant difference in their dissociation constants. The constancy of the values for the distribution constant of selenoyl-2-acetone and benzoylacetone over a fairly wide concentration range of the reagents in the organic solvent, for the various systems, testifies to the absence of association of reagent molecules in both the aqueous and the organic phases (Fig. 5). Determination of the stability constants, and the distribution constants of the complex compounds of selenoyl-2-acetone and benzoylacetone with various metal ions will assist in assessing the values of these compounds as analytical reagents.

## SUMMARY


1. The absorption spectra of aqueous solutions of selenoyl-2-acetone and benzoylacetone at various hydrogen ion concentrations have been studied.

2. The dissociation constants of the reagents indicated have been determined for an ionic strength of the solution of 0.1; $pK_{dissoc.} = 8.55 \pm 0.08$ (selenoyl-2-acetone) and $pK_{dissoc.} = 8.96 \pm 0.09$ (benzoylacetone).

3. The distribution constants of these reagents have been determined in various systems ($25 \pm 0.1°$; $\mu = 0.1$).

a) Selenoyl-2-acetone — $\log K_{distrib.} = 2.922 \pm 0.006$ ($CHCl_3 - H_2O$ — phase).
$\log K_{distrib.} = 3.004 \pm 0.010$ ($C_6H_6 - H_2O$ — phase).

b) Benzoylacetone — $\log K_{distrib.} = 3.439 \pm 0.009$ ($CHCl_3 - H_2O$ — phase).
$\log K_{distrib.} = 3.145 \pm 0.010$ ($C_6H_6 - H_2O$ — phase).


## LITERATURE CITED


[1] J. Rydberg, Acta Chem. scand. 4,1503 (1950).

[2] J. Rydberg, Arkiv kemi 8, 101 (1955).

[3] Symposium "Organic Reactions" I, IL, Moscow, 1948, p. 124.*

[4] N. D. Pryanishnikov, "Practical Textbook on Organic Chemistry," [In Russian], Moscow, 1956.

[5] R. A. Morton, A. Hassan, and T. C.Calloway, J. Chem. Soc., 883 (1934).

[6] A. P. Zozulya, and V. M. Peshkova, J. Inorg. Chem. (In the press).

[7] W. Stenström and N. Goldsmith, J. Phys. Chem. 30, 1683 (1926).

[8] C. V. Banks and A. B. Carlson, Analyt. chim. acta 7, 291 (1952).

[9] D. Dyrssen, Acta chem. scand, 8, 1394 (1954).

[10] D. Dyrssen and E. Johansson, Acta chem. scand. 9, 763 (1955).

[11] L. Vareille, Bull. Soc. chim. France. N 6, 870 (1955).

[12] J. Tachi, Mem. Coll. Agr. Kyoto Imp. Univ. 42, chem. Ser., N 22, 65 (1938); C.A., 32, 56852.

[13] M. L. Eidinoff, J. Amer. Chem. Soc. 67, 2072 (1845).

[14] J. Rydberg, Svensk. kem. tidskr. 65, 37 (1953).



Received April 24, 1958


*Russian translation.

# THE USE OF A ROTATING PLATINUM MICRO-DISC ELECTRODE IN POLAROGRAPHIC ANALYSIS

M. B. Bardin, Yu. S. Lyalikov, and V. S. Temyanko

Kishinev State University

In recent years, in addition to further developments in the theory and practice of polarography with dropping electrodes, there has been a significant increase in the attention displayed by research workers to solid electrodes. Platinum wire electrodes — stationary and rotating — have found the widest application.

The stationary electrode possesses a number of disadvantages which depress its practical value, and limits its applicability. Accordingly, preference is given in analytical practice to the rotating electrode.

The choice of the shape of the electrode, including the wire electrode itself, has not hitherto been given a theoretical foundation. The wire electrode which was first suggested by Kolthoff as long ago as 1941 [1] has been adopted by many research workers, either with or without technical modifications, and has arbitrarily justified itself for solving a number of analytical or electrochemical problems. On the other hand, Levich [2] has given a general quantitative theory of the disc electrode. In the presence of an indifferent electrolyte, the diffusion current which is determined by the reduction of an uncharged particle or ion, is expressed by the equation:

$$i_d = 0{,}62\, n\, F D^{2/3} \omega^{1/2} \nu^{-1/6} c S, \qquad (1)$$

where n is the number of electrons participating in the reaction; F is the Faraday number; D is the diffusion coefficient in $cm^2$/second; $\omega$ is the angular rate of rotation equal to $2\pi m$, where m is the number of rotations of the electrode per second; $\nu$ is the kinematic viscosity of the liquid in $cm^2$/second; c is the concentration of the ions being reduced in moles/ml; and S is the area of the electrode surface in $cm^2$.

The Levich equation has been checked for the relation between the limiting current and the rotational rate of the electrode by Siver and Kabanov for laminar conditions [3], and by Bagotskaya for turbulent conditions [4]. The authors got good agreement between theory and practice. Siver and Kabanov [5], taking oxygen and hydrogen, found a similar agreement for the relation between the diffusion current and the diffusion coefficient. Hogge and Kraichman [6], and Fedorova and Vidovich [7] confirmed the theory taking the cathodic reduction of iodine as an example. These facts make the disc electrode very attractive for use in analytical practice, and challenges the critical observations of Heyrovskii [8] apropos the use of solid electrodes.

Possible reasons which hinder the practical adoption of the disc electrode, in our opinion, are the complexity of the construction proposed for this electrode, and its relatively large size. Consequent upon this is the rather large size of the apparatus, and the large volume of solution to be polarographed, which, naturally complicates operation. Were the disc electrode given a more practically convenient form, then it could successfully replace the traditional wire electrode, over which it would have undisputed advantages. We have described a disc electrode with such desirable features [9].

The subject of the present article is the study of the characteristics of the micro-disc electrode, and clarification of the possibility of using it for polarographic analysis.

In the work described here, a visual polarograph, and mirror galvanometers type M-21 and GZS with a constant of about $10^{-9}$ amp./mm were used. In order to avoid working with large amounts of mercury, glycerol or water was introduced into the rotating part of the setup described previously [10] to act as a seal;

contact was established by means of a copper brush (Fig. 1).

Before use, the micro-disc electrode (S = 0.78 $mm^2$) was polished with emery cloth and cleaned with damp filter paper; it was then washed with water; before introducing the electrode into the solution of ions to be reduced, it was subjected to cathodic polarization for 3-4 minutes in a cell containing 0.1 N hydrochloric or sulfuric acid, at the hydrogen discharge potential (for complete purification of the electrode surface from surface oxides, the presence of which, as pointed out by a number of authors [11-13], complicates the electrochemical process and leads to poorly defined polarographic waves). The anode was a platinum plate with a surface area S of 400 $mm^2$.

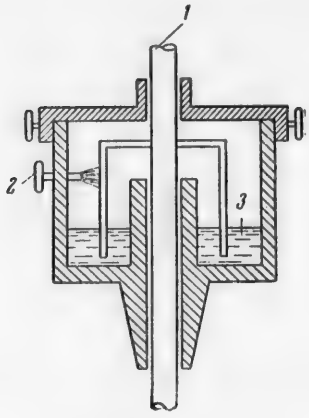



Fig. 1. Seal with rotating electrode, 1) rotating axis; 2) brush contact; 3) glycerol.

Clearly defined, and satisfactorily reproducible waves were obtained for oxygen, hydrogen ions, $[AuCl_4]^-$ and $[PtCl_6]^{2-}$ on the platinum micro-disc electrode (Fig. 2). The wave shown in Fig. 2 were obtained after the tenth cycle without purifying the electrode surface. In this case the maximum deviation from the mean value for the series of determinations did not exceed 3%. In order to get clearly defined and reproducible waves it is essential to center the electrode accurately; it was found necessary that the position of the electrode with respect to its axis did not change from test to test, a condition which it was not difficult to observe.

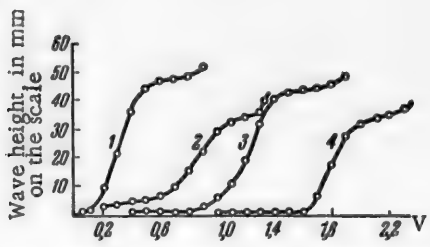



Fig. 2. Waves obtained on a micro-disc electrode. 1) $[AuCl_4]^-$ gold concentration $C_{Au}$ = 0.775 mg/25 ml, 1 mm on the scale = 0.09 $\mu$a, 800 revolutions/minute; 2) $[PtCl_6]^{2-}$ $C_{Pt}$ = 2.8 mg/25 ml, 1 mm scale = 0.36 $\mu$a, 800 revolutions/minute; 3) $O_2$ (saturated solution) 1 mm on the scale = 0.24 $\mu$A, 400 revolutions/minute; 4) $[H_3O]^+$ $C_H = 4 \times 10^{-3}$ $NH_4Cl$, 1 mm on the scale = 2.20 $\mu$A, 335 revolutions/minute, supporting electrolyte 0.1 N $NaNO_3$.

In order to verify Levich's equation, the relationship between the diffusion current and the rate of rotation of the electrode was studied. The work was carried out in a supporting electrolyte of 0.1 N $NaNO_3$ at room temperature (20 $\pm$ 1°). The following test materials were used: molecular oxygen, hydrogen ions, and $[AuCl_4]^-$. As is evident from Fig. 3, in agreement with theory, the diffusion current is proportional to the square root of the rotational rate of the electrode for all these test materials, including gold, in which case the electrode reactions are accompanied by deposition of metal on the electrode.

A direct proportionality was observed on the micro-disc electrode between the diffusion current and concentration. In Fig. 4 are shown calibration curves we took for hydrogen ions; the calibration curve for gold has been given previously [9].

Using equation (1), values of the diffusion current of hydrogen in a solution of $4 \times 10^{-4}$ N hydrochloric acid in a supporting electrolyte of 0.1 N $NaNO_3$ were calculated for various rotational speeds of the electrode. The value for the diffusion coefficient of hydrogen ions, taken from the work of Siver and Kabanov [5], was taken as being equal to $7.4 \times 10^{-5}$ $cm^2$/sec, while the value assumed for the viscosity was $10^{-2}$ $cm^2$/sec. Results of these calculations are given in Table 1.

In evaluating the results obtained it should be borne in mind that the value of the diffusion coefficient which we used holds for several other conditions, and that we did not succeed in achieving strict centering of the electrode. Taking these facts into account, and also the small value of the electrode surface, the agreement obtained between the experimental and theoretical values can be regarded as satisfactory.

On the basis of the experimental results which we obtained for gold, an attempt was made, using equation (1), to calculate the value of the diffusion coefficient for $[AuCl_4]^-$ ions in a supporting electrolyte of

0.1 N $NaNO_3$. Results of these calculations are given in Table 2.

The value which we found for the diffusion coefficient of the $[AuCl_4]^-$ ion (Table 2) is in satisfactory agreement with the value of $1.04 \times 10^{-5}$ $cm^2/sec^{-1}$, found by other authors by means of a dropping electrode and using the Il'kovich Equation [15].

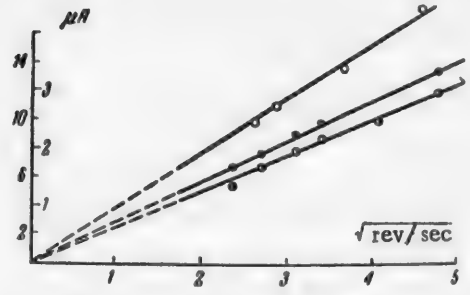



Fig. 3. The relation between the diffusion current and the rotational speed of the micro-disc electrode. O) oxygen, saturated solution, ⊙) hydrogen $4 \times 10^{-4}$ N HCl; ⊕) gold, $1.6 \times 10^{-4}$ M, solution of $H[AuCl_4]$ (the values of 1-3 μ a relate to gold, supporting electrolyte 0.1 N $NaNO_3$).

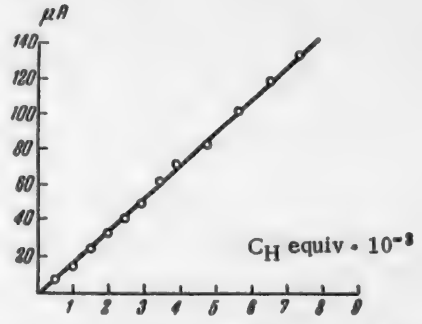



Fig. 4. Relation between diffusion current and hydrogen ion concentration.

As our experiments showed, the micro disc can also be used for polarography in a flow stream. The possibility of carrying out polarographic analysis in a flow has been investigated by Wilson and Smith [14] using a dropping mercury electrode. A solid micro-disc electrode may prove better for this purpose, particularly when it is considered in conjunction with automation of control.

TABLE 1

| m = rev per sec | $\omega = 2\pi m$ | $\omega^{\frac{1}{2}}$ | $i_d$, calc., in μA | $i_d$ found exp. in μA | Deviation, in % |
|---|---|---|---|---|---|
| 5,60 | 35,2 | 5,94 | 8,3 | 7,4 | 10,5 |
| 7,25 | 45,5 | 6,75 | 9,4 | 7,7 | 18,0 |
| 9,60 | 60,3 | 7,76 | 10,8 | 9,1 | 15,5 |
| 11,75 | 73,8 | 8,60 | 12,0 | 9,85 | 18,0 |
| 22,75 | 142,0 | 11,90 | 16,6 | 13,9 | 16,0 |

The platinum micro-disc electrode has a number of advantages over the wire electrode. The first is simpler to handle. Periodical chemical or mechanical cleaning of the wire electrode (for removal of electrode reaction products from its surface) leads to fairly rapid corrosion of the electrode and to breakage. A micro-disc electrode can be cleaned much more easily, particularly by light polishing on a file or on fine emery paper. This leads to complete renewal of the electrode surface without destroying its completeness, thanks to which its period of service is much longer.

TABLE 2

| $\omega^{\frac{1}{2}}$ | $i_d$, in μA | $D[AuCl_4]^-$ in $cm^2/sec \cdot 10^5$ |
|---|---|---|
| 5,94 | 1,35 | 1,04 |
| 6,75 | 1,70 | 1,20 |
| 7,76 | 1,98 | 1,24 |
| 2,60 | 2,16 | 1,21 |
| 10,10 | 2,52 | 1,19 |
| 11,90 | 3,15 | 1,27 |
| | Mean | 1,19 |

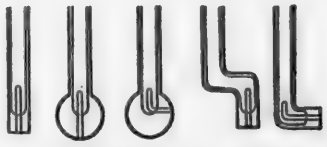


Fig. 5. Forms of the micro-disc electrode.

Moreover, it should be noted that by making the glass sheath of the electrode in various shapes (Fig. 5), it is possible to modify the diffusion conditions and the stirring conditions.

## SUMMARY

The possibility of using a rotating micro-disc electrode in polarographic analysis has been investigated. In accordance with Levich's equation, diffusion currents on the micro-disc electrode are proportional to the concentration and to the square root of the rotational speed of the electrode; the values found theoretically for the diffusion currents are in satisfactory agreement with those found experimentally. Using Levich's equation as a basis, the diffusion coefficient of the $[AuCl_4]^-$ ions was calculated (the supporting electrolyte used was 0.1 $NaNO_3$); it was found to be $1.2 \times 10^{-5}$ $cm^2/sec$.

Micro-disc electrodes can be used instead of wire electrodes in polarographic analysis.

## LITERATURE CITED

[1] I. M. Kolthoff and J. Lingane, "Polarography" [Translated from English] Goskhimizdat, Moscow-Leningrad, 1948.

[2] B. G. Levich, "Physicochemical Hydrodynamics", [In Russian], Acad. Sci. USSR, Moscow, 1952.

[3] Yu. G. Siver and B. N. Kabanov, J. Phys. Chem. 22, 53 (1948).

[4] I. A. Bagotskaya, Proc. Acad. Sci. 85, 1057, (1952).

[5] Yu. G. Siver and B. N. Kabanov, J. Phys. Chem. 23, 428 (1949).

[6] E. Hogge and M. Kraichman, J. Amer. Chem. Soc. 76, 1431 (1954).

[7] A. I. Fedorova and G. A. Vidovich, Proc. Acad. Sci. 109, 135 (1956).

[8] Ya. Heyrovskii, Industrial Labs. 23, 388 (1957).

[9] M. B. Bardin, B. S. Temyahko and Yu. S. Lyalikov, J. Anal. Chem. (In the press).

[10] M. B. Bardin and Yu. S. Lyalikov, J. Anal. Chem. 11, 704 (1956).

[11] M. B. Bardin, Candidate's Thesis, Kishinev, 1955 [in Russian].

[12] I. Kolthoff and N. Tanaka, Analyt. Chem 26, 632 (1954).

[13] D. Ferrett and C. Phillips, Trans. Faraday Soc. 51, 387 (1955).

[14] L. Wilson and R. Smith, Analyt. Chem. 25 218 334 (1953).

[15] R. Simpson, R. Evans, and H. Saroff, J. Amer. Chem. Soc. 77, 1438 (1955).

Received September 27, 1957

# A STUDY OF THE ANALYTICAL CHEMISTRY OF THALLIUM
# COMMUNICATION 2. PRECIPITATION REACTIONS OF THE BROMIDE COMPLEXES OF TRIVALENT THALLIUM WITH CERTAIN PYRAZOLONE DERIVATIVES*

A. I. Busev and V. G. Tiptsova

The M. V. Lomonosov Moscow State University

On the basis of the values for the normal oxidation–reduction potentials $E_0 Tl^{3+}/Tl^+ = 1.22$ volt and $E_0 Br_2/Br^- = 1.066$ volt [1], it might be assumed that trivalent thallium ions would oxidize bromine ions, even though only partially, to elemental bromine. Nevertheless, even qualitative tests show that in acid solution (2 N $H_2SO_4$) this reaction does not occur. This fact can be explained on the basis that trivalent thallium ions form stable complex ions with bromine, as a result of which the oxidation potential of the system $Tl^{3+}/Tl^+$ drops sharply. Benoit [2] using a potentiometric method found the following pK values: 9.7 for $TlBr^{2+}$, 6.9 for $TlBr_2^+$, 4.6 for $TlBr_3$, 2.7 for $TlBr_4^-$. Peshanskaya and Vallada-Dubois [3], on the basis of spectrophotometric and potentiometric measurements, have concluded that in solutions containing $Tl^{3+}$ and $Br^-$, the following complex ions exist: $TlBr^{2+}$ ($pK_1$ 8.9), $TlBr_2^+$, ($pK_2$ 7.5), $TlBr_3$ ($pK_3$ 5.7), $TlBr_4^-$ ($pK_4$ 4), $TlBr_5^{2-}$ ($pK_5$ 3.1), $TlBr_6^{3-}$ ($pK_6$ 2.4). The values found for pK show that the bromide complexes of thallium are quite stable, the stability decreasing with increasing coordination number.**

It has been established that $Tl^{3+}$ ions, in the presence of $Br^-$ and $Cl^-$ ions, interact with basic dyes to give sparingly soluble compounds. Thus, Feigl and co-workers [5] have shown that the bromide and chloride complexes of thallium form red-violet precipitates with the basic dye rhodamine B; these precipitates can be extracted with organic solvents to give intensely red-colored extracts; the reagent itself is not extracted. A similar color reaction is given in weakly acid solutions by the complex anions $TlCl_4^-$ and $TlBr_4^-$ with methyl-violet [6, 7] and other basic dyes of the diaminotriphenylmethane series [8, 9]. A method has been developed for separating $10^{-6}$ – $10^{-7}$% Tl based on the coprecipitation of $TlCl_4^-$ with a precipitate formed by p-dimethylaminoazobenzene and sodium p-dimethylaminoazobenzene-p-sulfonate [10]. There are published references [11, 12] to the detection of univalent thallium by means of a very sensitive reaction based on the formation of characteristic crystals by the action of a solution containing sodium iodide and iodine (oxidizing agent) in the presence of concentrated hydrochloric acid and several alkaloids, and also in the presence of certain nitrogen-containing organic bases (quinoline, antipyrine, pyramidone, and urotropine).

Our experiments have shown that, under certain conditions, trivalent thallium in the presence of bromine ions is precipitated by pyrazolone derivatives: antipyrine (1-phenyl-2,3-dimethylpyrazolone), pyramidone (dimethylaminoantipyrine), diantipyrylmethane, and diantipyrylphenylmethane.

---

*For Communication 1, see J. Anal. Chem. 13, 180 (1958). Original Russian pagination. See C.B. Translation.

**The bromide complexes of trivalent thallium are stable enough to permit amperometric titration of $Tl^{3+}$ ions with potassium bromide. Songina [4] has carried out such a titration. Nevertheless, on the basis of a comparison of the oxidation–reduction potentials, she erroneously suggested that the reaction: $Tl^{3+} + 2Br^- \rightarrow Tl^+ + Br_2$ forms the basis of the method she had developed. Experiments show that under the titration conditions used in Songina's method, liberation of elemental bromine is not observed.

The aim of our work was the study of the precipitation reactions of the bromide complexes of thallium with certain pyrazolone derivatives from the point of view of the analytical application of such reactions. Accordingly, we were interested in the properties of the compounds formed, their composition, their suitability for gravimetric purposes, and the possibility of developing methods for the amperometric titration of thallium.

## 1. Precipitation of Trivalent Thallium in the Presence of Bromide Ions with Pyramidone

On addition of an aqueous solution of pyramidone to an acid solution containing $Tl^{3+}$ ions and an excess of bromide ions, there is formed a white, clotted precipitate with a yellow tinge. In order to study the properties and composition of the precipitate the latter was isolated and analyzed.

For preparation of the bromide complex of thallium with pyramidone, about 0.5 g of $TlNO_3$ dissolved in 1 N $H_2SO_4$ was oxidized with $(NH_4)_2S_2O_8$; to the solution thus obtained was added 5 ml of a 40% solution of HBr, and 0.5 g of pyramidone dissolved in dilute $H_2SO_4$. The yellowish-white material which was formed was filtered off, and then washed 2-3 times with water. On crystallizing from acetone, large crystals with a bright-yellow color and in the form of right hexahedrons, were obtained. The crystals melted at 185° with decomposition.

In weakly acid solution, trivalent thallium oxidizes pyramidone to form an intensely blue-violet colored solution; the color is not stable, but the color effect produced can serve for the qualitative detection of $Tl^{3+}$ in the absence of an oxidizing agent. $Tl^{3+}$ can be detected as follows: to 2-5 ml of a weakly acid solution (pH 3-4, in the absence of $Cl^-$ and $Br^-$ ions) is added 1 ml of a saturated solution of pyramidone. Immediately, or almost immediately, there appears a blue-violet color which disappears on standing. Limit of identification 4 γ/ml.

Independently from us, the oxidation of pyramidone by trivalent thallium was used by Kamemoto [13] for the photometric determination of 1-5 mg of Tl in 50 ml of solution at 510 mμ. He showed that at pH 4.0, the color gradually changes from violet to red, and after 60 minutes becomes almost constant. At considerably lower Tl concentrations we did not observe this change of color to red, since it is several times less intense than the colors observed by Kamemoto. In the presence of large amounts of $Cl^-$ and $Br^-$, at pH 4-5, the color is accompanied by the formation of a precipitate, nevertheless, its intensity is less than in the case where $Cl^-$ and $Br^-$ are absent. The pH value at which the color appears in the presence of $Cl^-$ and $Br^-$ is somewhat higher than in their absence.

The compound formed between thallium and pyramidone was analyzed for its Br and Tl contents. Bromine was determined, after dissolving an exact aliquot of the material in acetone, by precipitation with $AgNO_3$ and weighing the AgBr formed. Thallium was determined gravimetrically as TlI; an aliquot of the test material was dissolved in a small amount of acetone, about 0.1 g of KI was added and a few ml of 5% $Na_2S_2O_3$ then added until the yellow color of the solution disappeared; the solution plus precipitate was then allowed to stand overnight; the precipitate was filtered through a No. 3 glass crucible, washed with 80% acetone, and finally dried at 120-130° and weighed.

Found: Br 41.88; 42.45; 42.10%; Tl — 27.17; 26.90; 26.72%. Calculated for $C_{13}H_{17}ON_3 \cdot HTlBr_4$: Br — 42.26%; Tl — 27.02%.

On the basis of the results obtained it can be postulated that the reaction proceeds according to the following equation:

$$C_{13}H_{17}ON_3 + Tl^{3+} + 4Br^- + H^+ \rightarrow C_{13}H_{17}ON_3 \cdot HTlBr_4.$$

Despite the relatively high molecular weight of tetrabromothalliumpyramidone (756.4) and the favorable conversion factor to Tl (F = 0.2702), this compound is not suitable for the quantitative determination of thallium because of its appreciable solubility in water. Thallium is not quantitatively precipitated at very high concentrations of bromide and pyramidone. The thallium compound is soluble in many organic solvents: acetone, ethanol, chloroform, carbon tetrachloride, etc.

## 2. Precipitation of Trivalent Thallium in the Presence of Bromide Ions with Antipyrine

Thallium is precipitated by antipyrine from an acid solution, at sufficiently high bromide concentrations, in the form of a finely dispersed turbidity; crystals appear on agitation. The crystals, which are almost colorless when they are formed, become greenish-yellow after filtration and drying. The material is appreciably soluble in water, alcohol, and ether; it is readily soluble in acetone and chloroform, and insoluble in excess precipitant. On recrystallizing from acetone, yellowish needles which melt at 129-130° are formed.

The compound was synthesized by the same method as that described in the previous case. In addition to determining Br and Tl, the molar ratio of $Tl^{III}$: antipyrine was established by determining the excess antipyrine in solution after precipitation of an exactly known amount of Tl by a known amount of antipyrine. This was done as follows: to a solution of 17.90 mg of $Tl^+$ contained in a 50 ml standard flask was added 2 ml of 2 M KBr, 2 ml of $HNO_3$ (1 : 1), and 3 ml of 0.1 N $KBrO_3$; excess bromine was removed by addition of 1-2 drops of a 10% solution of sulfosalicylic acid; 10 ml of 0.1044 M antipyrine solution containing 1 mole/liter of KBr was then added and the solution made up to the mark. The following day the precipitate was filtered off through a dry filter into a dry beaker. Antipyrine was determined in the filtrate by a somewhat modified Gusev method [14], an aliquot (10 ml) of the solution was transferred to a dry beaker, and 10 ml of 0.02357 M $K_4Fe(CN)_6$ and 10 ml of 1 N $H_2SO_4$ added. After mixing the whole thoroughly, it was allowed to stand for 10-15 minutes and the solution then filtered through a dry filter into a dry beaker. 15 ml of this filtrate was taken for titration, this volume was diluted with water to 50-75 ml and then 1-2 ml of 1% $K_3Fe(CN)_6$ added and the solution titrated potentiometrically with a standard $ZnCl_2$ solution. In this way excess ferrocyanide was determined, and from this the amount of antipyrine in the solution above the precipitate of the bromide complex of thallium with antipyrine. The antipyrine solution was also standarized by the ferrocyanide method. In two such experiments 0.1965 g of antipyrine and 0.0179 of Tl were taken in each case. The excess antipyrine found was 0.1646 and 0.1609 g. These values correspond to molar ratios of Tl : $C_{11}H_{12}ON_2$ of 1 : 1.94 and 1 : 2.16. It can be assumed therefore that 1 mole of Tl is associated in the complex with 2 moles of antipyrine.

The bromine content of the compound obtained was determined by weighing the bromine as AgBr, and also by potentiometric titration of the solution obtained by dissolving the material in a 1 : 1 mixture of water and acetone, using silver nitrate as the titrant and using a silver electrode.

Found: Br 35.89 (potentiometrically) 35.49; 35.62 (gravimetrically) Tl 22.60; 22.14% (gravimetrically)
Calculated: for $(C_{11}H_{12}ON_2)_2HTlBr_4$: Br — 35.46%; Tl — 22.68%.

Thus, the reaction proceeds according to the equation:

$$2C_{11}H_{12}ON_2 + H^+ + 4Br^- + \rightarrow (C_{11}H_{12}ON_2)_2 \cdot HTlBr_4.$$

Gravimetric determination of Tl by precipitation and weighing as $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$ was carried out as follows: to the solution containing $Tl^+$ was added 5 ml of $HNO_3$ (1 : 1), a few ml of 0.01 N $KBrO_3$ (1 ml per 10 mg Tl), and 10 ml of 2 M KBr; excess bromine was removed by addition of a 10% solution of sulfosalicylic acid; 10-15 ml of 0.1 M antipyrine was then added slowly with sitrring. The total volume amounted to 40-50 ml. After standing for a short time the precipitate was filtered through a No. 3 glass filter, and washed 2-3 times, first with a solution of precipitant, and then with a saturated solution of the compound formed; the precipitate was finally dried at 105-110°. The precipitate was not hygroscopic and reached constant weight after 1 hour.

The method gives results which are systematically 2-3% low (Table 1), probably because of the appreciable solubility of the precipitate under the experimental conditions used. In the absence of excess precipitant the precipitate is appreciably soluble; accordingly, amperometric titration of the bromide complex of thallium with a solution of antipyrine is not possible.

## 3. Precipitation of Trivalent Thallium in the Presence of Bromide By Means of Diantipyrylmethane

On the assumption that the solubility of a compound decreases with increasing molecular weight, we hoped that we would get more satisfactory results by using diantipyrylmethane, which has a higher molecular weight, for precipitating the bromide complex of thallium.

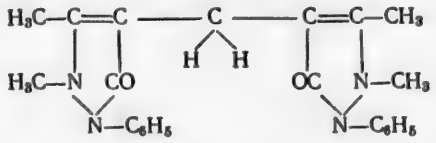
The reagent was synthesized by Zhivopistsev's method [15]. It was purified as follows: about 2 g of material was dissolved in 200 ml water on addition of 3-4 ml of concentrated HCl, and the solution obtained was neutralized with $NH_4OH$ (1 : 1) while stirring. The precipitated base was filtered, and then washed until it gave a negative test for chloride ions. The purified crystallohydrate had a melting point of 143°. A 1% solu-

TABLE 1

Gravimetric Determination of Thallium as $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$

| Weight of precipitate of $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$ | Tl taken, in mg | Tl found, in mg | Error | |
|---|---|---|---|---|
| | | | in mg | in % |
| 119,7 | 26,8 | 27,2 | +0,4 | +1,5 |
| 119,0 | 26,8 | 27,0 | +0,2 | +0,7 |
| 152,1 | 35,8 | 34,5 | +1,3 | −3,6 |
| 153,6 | 35,8 | 34,8 | −1,0 | −3,0 |
| 191,8 | 44,7 | 43,5 | −1,2 | −2,7 |
| 197,3 | 44,7 | 44,8 | +0,1 | +0,2 |
| 77,5 | 17,7 | 17,6 | −0,1 | −0,6 |
| 76,8 | 17,7 | 17,4 | −0,3 | −1,8 |
| 57,3 | 13,3 | 13,0 | −0,3 | −2,3 |
| 37,5 | 8,84 | 8,50 | −0,34 | −3,8 |
| 39,3 | 8,84 | 8,93 | +0,09 | +0,1 |

tion of the reagent in 0.5 N $H_2SO_4$ containing 1% of HBr (by weight) was used for gravimetric determinations: 1 ml of this solution precipitates about 5 mg of Tl. A 0.1% solution of diantipyrylmethane, prepared by dissolving an exactly weighed aliquot of the reagent dried to constant weight at 105-110°, was used for amperometric titration. The solution was standardized by means of an iodometric method similar to that used by Kumov [16] for determination of antipyrine, since the molecule of diantipyrylmethane.



contains two atoms of hydrogen which can be replaced by iodine. For this purpose, 10 ml of 0.005 N $I_2$ and 0.1 g of $CH_3COONa$ were added to 5 ml of the diantipyrylmethane solution; after 3-5 minutes excess iodine was titrated amperometrically at 0 volt with 0.005 N $Na_2S_2O_3$ until the iodine current disappeared. It was found that 1 ml of this solution contained 0.7997 mg of antipyrylmethane, or based on the aliquot taken, 1 ml of this solution contained 0.8010 mg.

We established that diantipyrylmethane quantitatively precipitates thallium from solutions containing bromide ions. The clotted precipitate formed externally resembles silver bromide; on agitation it rapidly coagulates.

In order to determine the composition of the bromide complex of thallium with diantipyrylmethane, a solution containing a known amount of $Tl^{3+}$ was titrated amperometrically at a sufficient concentration of bromide ions (1 mole/liter KBr) with an accurately prepared solution of diantipyrylmethane. The equivalence point was established by the disappearance of the reduction current of thallium on a rotating platinum microelectrode at a potential of 0.0 v with respect to the saturated calomel electrode (Fig. 1, a,b). Titration results (Table 2) showed that diantipyrylmethane and thallium —as its bromide complex—react in a molar ratio approximating to unity.

The bromine content of the synthesized compound was determined by potentiometric titration of an aliquot of the compound, dissolved in 9 : 1 mixture of acetone and water, with silver nitrate. Thallium was

determined by complexometric titration, after decomposition of an aliquot of the compound with concentrated $H_2SO_4$ in the presence of $H_2O_2$, using 1-(2-pyrydylazo)-2-naphthol as indicator [17].

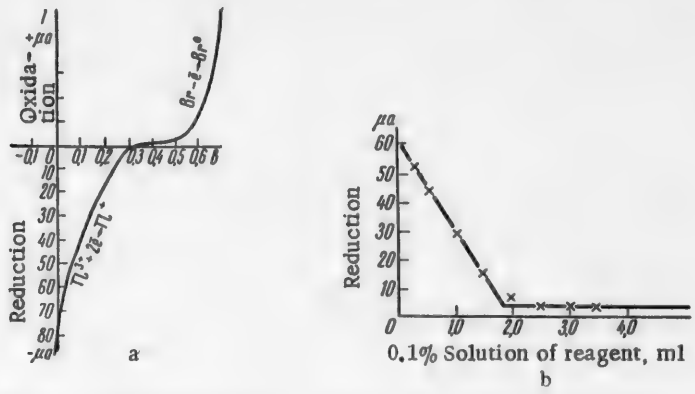



Fig. 1. a) Current-voltage curve for $1.25 \times 10^{-3}$ N $Tl_2(SO_4)_3$ in a supporting electrolyte of 1 M KBr; b) Amperometric titration curve for the bromide complex of trivalent thallium with a solution of diantipyrylmethane.

Found: Br 34.57; 34.81%; Tl 22.36; 22.43%. Calculated for $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$; Br 34, 98%, Tl 22.38%.

Accordingly, the composition of the bromide complex with diantipyrylmethane corresponds to the formula:

$$C_{23}H_{24}O_2N_2 \cdot HTlBr_4.$$

Gravimetric determination of thallium by precipitation and weighing as $C_{23}H_{24}O_2N_2 \cdot HTlBr_4$ was carried out as follows: to an acid solution of $Tl^{3+}$ sulfate or nitrate was added a 1% solution of the reagent and some HBr (1-2 ml for each 5 mg of Tl); the precipitate was filtered through a No. 3 glass filter and washed with HBr solution (1 : 100); it was then dried at 100-120° to constant weight. The results are given in Table 3. The conversion factor to thallium is 0.2238.

TABLE 2

Molar Ratios of Diantipyrylmethane and Thallium

| Thallium taken | | | Diantipyrylmethane used | | | Molar ratio $Tl^{III}$ : $C_{23}H_{24}O_2N_2$ |
|---|---|---|---|---|---|---|
| ml (0.262 mg/ml) | in mg | mmoles ($\times 10^{-3}$) | ml (0.01 mg/ml) | in mg | mmoles ($\times 10^{-3}$) | |
| 2,00 | 0,524 | 2,56 | 1,15 | 0,921 | 2,37 | 1 : 0,9 |
| 3,00 | 0,786 | 3,85 | 1,90 | 0,522 | 3,83 | 1 : 1,0 |
| 3,00 | 0,786 | 3,85 | 1,90 | 1,522 | 3,83 | 1 : 1,0 |
| 5,00 | 1,310 | 6,42 | 3,10 | 2,483 | 6,40 | 1 : 1,0 |
| 5,00 | 1,310 | 6,42 | 3,15 | 2,528 | 6,52 | 1 : 1,0 |
| 5,00 | 1,310 | 6,42 | 3,12 | 2,500 | 6,44 | 1 : 1,0 |

Elements such as zinc and copper, which do not form stable bromide complexes, do not cause any difficulty during the determination of thallium, since they are not precipitated by diantipyrylmethane. It is known, however, [17] that at relatively high bromide concentrations cadmium reacts with the reagent. Nevertheless, in the absence of excess bromide ions, this metal is found in the form of the bromide complexes $CdBr^+$ and $CdBr_2$ which are not precipitated by diantipyrylmethane. Experiments showed that thallium can be determined in the presence of fairly large amounts of cadmium (Table 4), as long as precipitation is carried out from solutions

free from bromide ions, by adding the reagent and HBr in amounts which are twice the theoretical amounts necessary for forming $TlBr_4^-$ ions. Bismuth, even under these conditions, is coprecipitated with thallium to a considerable extent as a consequence of the higher stability of its bromide complexes as compared with those of the cadmium complexes; at a certain chloride concentration, bismuth is precipitated quantitatively by diantipyrylmethane [18]. By making use of the higher stability of the complex compound of bismuth with Complexon III as compared with the stability of its bromide complexes, we developed a technique for the deter-

TABLE 3

Gravimetric Determination of Thallium as $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$

| Wt. of the precipitate $C_{23}H_{24}O_2N_2 \cdot HTlBr_4$ | Tl taken, in mg | Tl found, in mg | Error, in mg | Wt. of the precipitate $C_{23}H_{24}O_2N_2 \cdot HTlBr_4$ | Tl taken, in mg | Tl found, in mg | Error, in mg |
|---|---|---|---|---|---|---|---|
| 203,7 | 45,7 | 45,6 | −0,1 | 77,6 | 17,4 | 17,4 | 0 |
| 201,5 | 45,7 | 45,1 | −0,6 | 77,3 | 17,4 | 17,3 | −0,1 |
| 206,0 | 45,7 | 46,1 | +0,4 | 38,8 | 8,70 | 8,69 | −0,01 |
| 116,3 | 26,0 | 26,0 | 0 | 38,3 | 8,70 | 8,57 | −0,13 |
| 115,9 | 26,0 | 25,9 | −0,1 | 39,3 | 8,70 | 8,80 | +0,10 |
| 117,4 | 26,0 | 26,3 | +0,3 | 35,1 | 7,84 | 7,86 | +0,02 |
| | | | | 35,0 | 7,84 | 7,84 | 0 |

mination of $Tl^{3+}$ in the presence of bismuth, in which the bromide complex of thallium was precipitated with diantipyrylmethane in the presence of Complexon III in a weakly acid medium (pH about 2). To the solution containing $Tl^{3+}$ and $Br^{3+}$ was added a few ml of a 5% Complexon III solution (1 ml per 20 mg), this was followed by addition of ammonia until the solution had a weak odor of the latter (if, at this stage, a turbidity should appear, some more Complexon III should be added), the necessary amount of reagent was then added and the solution carefully acidified with 2 N $H_2SO_4$ until the color of tropeoline 00 changed from yellow to orange red; the precipitate formed was washed twice with 0.5% Complexon III solution and then 2-3 times with HBr (1 ; 100)

TABLE 4

Gravimetric Determination of Thallium in the Presence of Zinc, Copper, Cadmium, Bismuth, and Antimony

| Tl taken, in mg | Added, in mg | | Tl found, in mg | Ratio Tl : Me | Tl taken, in mg | Added, in mg | | Tl found, in mg | Ratio Tl : Me |
|---|---|---|---|---|---|---|---|---|---|
| 9,15 | 575 | Zn | 9,11 | 1 : 60 | 9,15 | 3067 | Cd | 9,11 | 1 : 343 |
| 7,32 | 1977 | Zn | 7,50 | 1 : 200 | 7,32 | 80 | Bi | 7,25 | 1 : 10 |
| 9,15 | 1786 | Cu | 9,25 | 1 : 195 | 7,32 | 230 | Bi | 7,19 | 1 : 100 |
| 7,32 | 1786 | Cu | 7,38 | 1 : 244 | 7,32 | 100 | Sb | 7,43 | 1 : 14 |
| 9,15 | 86 | Cd | 9,02 | 1 : 10 | 6,40 | 100 | Sb | 6,49 | 1 : 15 |
| 9,15 | 1276 | Cd | 9,20 | 1 : 139 | 9,15 | 200 | Sb | 9,16 | 1 : 22 |
| 7,32 | 3067 | Cd | 7,36 | 1 : 419 | | | | | |

solution. The method gave satisfactory results (Table 4). In order to prevent interference from $Sb^V$ which forms stable bromide complexes which are precipitated by diantipyrylmethane, the antimony was complexed with tartaric acid; this complex is stable during subsequent acidification. This technique permits determination of thallium in the presence of antimony (Table 4).

Among those elements which interfere is $Fe^{III}$ which forms an intensely red colored solution with the reagent; the thallium precipitate is accordingly heavily contaminated with iron. Interference from iron can be avoided by precipitating thallium from a weakly acid solution containing the necessary amount of Complexon III for complexing the iron.

Determination of thallium in the presence of iron was carried out as follows: to the solution containing $Tl^{III}$ and $Fe^{III}$ was added a 5% solution of Complexon III (5 ml per 30 mg Fe), this was followed by addition of $NH_4OH$ until the appearance of a dark-red color, this is a sign of the complete complexing of iron by Complexon III; a few drops of 1 N $H_2SO_4$ was then added until the red color of the liquid changed to orange, about 5 ml of

TABLE 5

Gravimetric Determination of Thallium in the Presence of Iron

| Tl taken, in mg | Tl found, in mg | Fe added, in mg | Ratio Tl:Fe | Tl taken, in mg | Tl found, in mg | Fe added, in mg | Ratio Tl:Fe |
|---|---|---|---|---|---|---|---|
| 7,42 | 7,48 | 20 | 1 : 3 | 7,32* | 7,40 | 200 | 1 : 28 |
| 8,24 | 8,39 | 40 | 1 : 5 | 6,40* | 6,31 | 200 | 1 : 30 |
| 8,24 | 8,30 | 40 | 1 : 5 | 6,40* | 6,34 | 320 | 1 : 50 |
| 7,32 | 7,23 | 75 | 1 : 10 | 6,40* | 6,18 | 400 | 1 : 62 |
| 7,32 | 7,49 | 100 | 1 ; 14 | | | | |

*The thallium was reprecipitated.

reagent solution was next added with stirring, finally, 10 N $H_2SO_4$ was added dropwise until precipitate had ceased to separate out (it cannot be assumed that the appearance of a red color testifies to the decomposition of iron complexonate). For ratios of Tl : Fe > 1 : 10, precipitation must be repeated. For this purpose the precipitate was washed with dilute HBr (1 : 100), containing 0.5% Complexon III, the precipitate was then washed

TABLE 6

Amperometric Determination of Thallium (volume of solution 15 ml)

| Tl taken, in mg | Tl found, in mg | Error | | KBr concentration, in mole/liter |
|---|---|---|---|---|
| | | mg | % | |
| 1,05 | 1,05 | 0 | 0 | 1,0 |
| 1,05 | 1,05 | 0 | 0 | 0,002 |
| 1,31 | 1,31 | 0 | 0 | 1,3 |
| 1,31 | 1,29 | −0,02 | −1,5 | 1,3 |
| 0,66 | 0,68 | +0,02 | +3,0 | Saturated solution |
| 0,66 | 0,65 | −0,01 | −1,5 | 1,7 |
| 0,52 | 0,50 | −0,02 | −4,0 | 1,6 |
| 0,92 | 0,89 | −0,03 | −3,3 | 1,5 |
| 0,92 | 0,92 | 0 | 0 | 0,1 |
| 0,92 | 0,90 | −0,02 | −2,2 | Saturated solution |
| 1,31 | 1,32 | +0,01 | +0,8 | |
| 1,31 | 1,30 | −0,01 | −0,8 | 0,002 |

off the filter with 50-75 ml of an ammoniacal solution of Complexon III having a pH of 8-9, 5 ml of reagent was added and the solution acidified with 10 N $H_2SO_4$; under these conditions an absolutely white flocculent precipitate was obtained, this was filtered off, washed, dried, and weighed (Table 5).

In addition to determining thallium gravimetrically by means of this reagent, it is also possible to determine it amperometrically under the conditions described above. Changes in potassium bromide over a wide range have no effect on the titration results, titration can be carried out both in a saturated solution of KBr, and in a solution containing KBr in an amount of only 30-50% greater than that theoretically necessary for formation of $TlBr_4^-$ ions (Table 6).

Thallobromic acid is obviously a strong acid, since the solubility of its salts with diantipyrylmethane does not change appreciably with increasing $H_2SO_4$ concentration, and titration can accordingly be carried out

in strongly acid solutions (Table 7). Cadmium present to the extent of ten times that of thallium does not interfere with determination of the latter, as long as the bromide ion concentration is not greater than 0.1 M; similarly, no interference is shown by copper, zinc, bismuth, and iron, when the latter is complexed by means of Complexon III (or, not quite so well, with fluoride ions) so as to eliminate interference from the cathodic current of the $Fe^{III}$ ion at 0 volt. Some results for amperometric titration are given in Table 8.

TABLE 7

Amperometric Determination of Thallium at Various $H_2SO_4$ Concentrations of the Solution

| Tl taken, in mg | Tl found, in mg | Error | | $H_2SO_4$ concentration, in mole/liter |
|---|---|---|---|---|
| | | in mg | in % | |
| 0.66 | 0.67 | +0.01 | +1.5 | 0.5 |
| 0.66 | 0.65 | −0.01 | −1.5 | 0.5 |
| 0.66 | 0.66 | 0 | 0 | 1.0 |
| 1.31 | 1.31 | 0 | 0 | 1.0 |
| 0.66 | 0.67 | +0.01 | +1.5 | 3.0 |
| 0.92 | 0.91 | −0.01 | −1.1 | 3.0 |
| 0.79 | 0.79 | 0 | 0 | 5.0 |
| 0.79 | 0.80 | +0.01 | +1.2 | 10.0 |

An increase in KBr concentration to a level higher than that indicated in Table 8 leads to appreciable coprecipitation of bismuth, and the results for thallium are much too high.

### 4. Precipitation of Trivalent Thallium in the Presence of Bromide Ions with Diantipyrylphenylmethane

The reagent was synthesized by Gusev's method [19]. The bromide complex of thallium with diantipyrylphenylmethane was synthesized as follows: an aliquot of $TlNO_3$ (0.5328 g) was dissolved in 50-100 ml of 1 N $H_2SO_4$, and the thallium oxidized with $(NH_4)_2S_2O_8$ (Excess of the oxidizing agent was removed by boiling); 5 ml of 40% HBr was then added, followed by 0.87 g of diantipyrylphenylmethane dissolved in 25 ml of glacial acetic acid. The bright-yellow precipitate which separated out was filtered off and washed with water. The precipitate was purified by recrystallization from a mixture of methanol and acetone. The recrystallized material was in the form of lemon-yellow needles. At temperatures greater than 220° the material darkened in color, but did not melt (pressumably decomposition occurred). The properties of the compound obtained were similar to those of the three compounds described above: $C_{13}H_{17}ON_3 \cdot HTlBr_4$, $(C_{11}H_{12}ON_2)_2 \cdot$ $\cdot HTlBr_4$, $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$.

TABLE 8

Amperometric Determination of Thallium in the Presence of Other Metals (in a supporting electrolyte of 2 N $H_2SO_4$)

| Tl taken, in mg | Me added, in mg | | Tl found, in mg | Error, in mg | KBr concentration, in mole/liter |
|---|---|---|---|---|---|
| 0,79 | 100 | Zn | 0,80 | +0,01 | 0,002 |
| 1,31 | 50 | Zn | 1,31 | 0 | 0,002 |
| 0,66 | 200 | Zn | 0,66 | 0 | 0,002 |
| 0,79 | 70 | Bi | 0,78 | −0,01 | 0,002 |
| 0,79 | 100 | Bi | 0,80 | +0,00 | 0,002 |
| 1,31 | 10 | Cd | 1,29 | −0,02 | 0,002 |
| 0,79 | 50 | Cd | 0,79 | 0 | 0,002 |
| 0,79 | 10 | Cd | 0,80 | +0,01 | 0,1 |
| 0,79 | 10 | Cd | 0,79 | 0 | 0,1 |
| 0,79 | 10 | Cd | 0,84 | +0,05 | 0,2 |
| 0,79 | 10 | Cd | 0,86 | +0,07 | 0,2 |
| 0,79 | 20 | Cd | 0,91 | +0,12 | 0,5 |

During an analysis of the recrystallized material it was found gravimetrically that its bromine content was 32.56 and 32.84%, while the thallium content was found to be 20.84 and 20.62% by a complexometric method. The theoretical bromine and thallium contents for $(C_{11}H_{11}ON_2)_2 CHC_6H_5 \cdot HTlBr_4$ were 32.29% Br, and 20.65% Tl.

An attempt was made to use this reagent for the gravimetric determination of thallium in which a 1% solution of diantipyrylphenylmethane in glacial acetic acid containing 1% HBr was used for precipitation. Satisfactory results were not obtained, however, because of the slight solubility of the reagent in water, and also because of the low solubility of the bromide of diantipyrylphenylmethane, as a result of which the latter is strongly coprecipitated with the precipitate of $(C_{11}H_{11}ON_2)_2CHC_6H_5 \cdot HTlBr_4$.

## SUMMARY

1. Trivalent thallium ions can be precipitated in the presence of bromide ions by pyramidone, antipyrine, diantipyrylmethane, and diantipyrylphenylmethaneto form compounds whose composition corresponds to the following formulas: $C_{13}H_{17}ON_2 \cdot HTlBr_4$, $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$, $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$, $(C_{11}H_{11}ON_2)_2CHC_6H_5 \cdot HTlBr_4$.

2. Some of the properties of the compounds listed above have been studied.

It has been shown that $C_{13}H_{17}ON_2 \cdot HTlBr_4$, $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$, $C_{29}H_{28}O_2N_4 \cdot HTlBr_4$ are not suitable for the determination of thallium; using $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$, however, it is possible to develop gravimetric and amperometric methods for determining thallium in the presence of other elements (Cu, Zn, Cd, Bi, Fe, and Sb).

## LITERATURE CITED

[1] Yu. Yu. Lur'e, "Reference Tables for Chemists," [in Russian] Goskhimizdat, Moscow-Leningrad, (1947).

[2] R. Benoit, Bull. soc. chim. France 16, 518 (1949).

[3] D. Peschanski and S. Vallada-Dubois, C.r. Acad. sci. 241, 1046 (1955).

[4] O. A. Songina and A. P. Voiloshnikova, Industrial Labs. 22, 19 (1956).

[5] F. Feigl, V. Gentil and D. Goldstein, Analyt. chim. acta 9, 393 (1953).

[6] S. D. Gur'ev, Collection of Papers of Gintsvetmet, No. 10, 371 (1955) [in Russian].

[7] G. G.Shemeleva, and V. I. Petrashen', Trans. Novocherkask Polytech. Inst. 31, 87 (1955).

[8] L. N. Lapin and V. O. Gein, Trans. Commission on Anal. Chem. Acad. Sci. USSR, 7, 217 (1956).

[9] N. T. Voskresenskaya, J. Anal. Chem. 11, 585 (1956).*

[10] V. I. Kuznetsov and G. V. Myasoedova, J. Anal. Chem. 10, 211 (1955).*

[11] H. Wachsmuth, Chim. analyt. 29, 276 (1947).

[12] B. Berisso, C. A. 43, 175 (1949).

[13] Y. Kamemoto, J. Chem. Soc. Japan. Pure Chem. Sec. 78, N 5, 604-607 (1957).

[14] S. I. Gusev, J. Anal. Chem. 4, 175 (1949).

[15] V. P. Zhivopistsev, Industrial Labs. 16, 1186 (1950).

[16] V. I. Kumov, J. Anal. Chem. 9, 229 (1954).*

[17] A. I. Busev and V. G. Tiptsova, J. Anal. Chem. 13, 180 (1958).*

[18] V. P. Zhivopistsev, Industrial Labs. 18, 1428 (1952).

[19] S. I. Gusev, R. G. Beiles, and E. V. Sokolova, J. Anal. Chem. 6, 43 (1951).

Received July 27, 1957

*Original Russian pagination. See C.B. Translation.

# THE POLAROGRAPHIC DETERMINATION OF INDIUM

A. T. Nizhnik and I. S. Chaus

Institute of General and Inorganic Chemistry. Acad. Sci. Ukrainian SSR, Kiev

Despite the fact that many methods have already been suggested for the quantitative determination of indium (spectrographic [1-3], titrimetric [4], colorimetric [5], polarographic [6], etc.), there is at the moment, no rapid and reliable method for the determination of this element; such a method is of particular importance for the technical production of indium, and for its determination in materials during the search for indium raw materials.*

The most widely used method is the polarographic method suggested by Aref'eva [7]; however, the chemical preparation of the solutions to be polarographed is very long, difficult, and incomplete.

In particular, according to Gurin's results [8], in order to achieve complete separation of cadmium from indium by means of ammonia, at least a threefold reprecipitation is necessary for ordinary industrial materials. At the same time it is essential to completely remove copper, and particularly cadmium, from the indium solution because of the nearness of their half-wave potential.

Various other methods have been suggested for preparing the solutions for polarographic determination of indium [9-11].

We should like to suggest an amalgam method for preparing the solutions for polarographing, for the determination of indium in production materials and wastes containing hundredth parts of a percent, and more, of indium. A characteristic feature of this technique is that during treatment of the original sulfuric acid solution of indium (at ordinary temperatures) with the zinc amalgam, all those elements which interfere with the polarographic determination of indium are removed, while the indium remains in solution. To the solution purified in this way is added 10% of its weight of sodium chloride and the indium then determined polarographically. Removal of indium from a number of elements, including tin and cadmium, in sulfuric acid solutions on a zinc amalgam, is based on the specific behavior of indium towards the sulfate ion.

In 1947, a study was made of the effect of chlorides on the value of the diffusion current for indium in sulfuric acid solutions [13]. It was established that addition of chloride ions until their concentration is 10% of the sulfuric acid solution, in which the polarographic wave for indium cannot be detected, ensures the normal reduction of indium ions and the appearance of its wave. Other research workers have observed the same phenomenon at various times: Kolthoff and Lingane [14], Babko, Polishchuk, and Volkova [15], Bukhman [16]. Seward [17] and Ensslin [18], in the system indium sulfate—sulfuric acid established that an acid sulfate of indium with the composition $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$ is formed. Muzyka [19] while studying the same system by electroconductivity, cryoscopic, and transport-number methods established the existence of the anion $[In(SO_4)_2]^-$ in solution. Aksel'rud [20] using a polarographic method, confirmed the existence of the indium anion $[In(SO_4)_2]^-$ in acid solutions. Thus, the reason for the slow reduction of indium ions from sulfuric acid solutions is the formation of complex indium anions, and the changes in the value of the reduction potential of the latter arising from this. Under such conditions, as we have established, this process is essentially independent of the nature of the cation (hydrogen or metal) in the sulfates taken (Table 1).

*For a review of methods of determining indium, see [6a].

The half-wave potential of indium in a hydrochloric acid solution is equal to −0.597 volt (with respect to the saturated calomel electrode), while in sulfuric acid it is −1.06 volt; the half-wave potential of cadmium

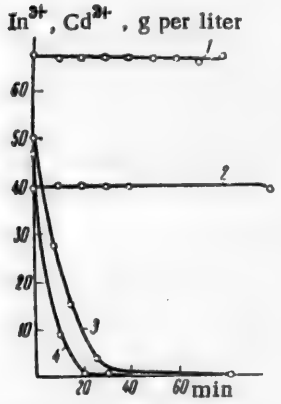
TABLE 1

Effect of the Concentration of $SO_4^{2-}$ Ions on the Extent of Reduction of Indium on a Zinc Amalgam

| In $H_2SO_4$ solutions | | In solutions of sulfates* | | |
|---|---|---|---|---|
| $H_2SO_4$ concentration, in % | Extent of the reduction of indium, in % | Sulfate taken | Concentration of $SO_4^{2-}$ ions, in % | Extent of the reduction of indium, in % |
| 3 | 12.1 | $(NH_4)_2SO_4$ | 20.0 | Not reduced |
| 6 | 9.5 | $MgSO_4$ | 19.9 | " |
| 10 | 5.8 | $MnSO_4$ | 20.2 | " |
| 15 | 2.4 | $ZnSO_4 \cdot 7H_2O$ | 21.0 | " |
| 20 | Not reduced | — | — | " |

*In order to avoid hydrolysis, about 1.5% of free sulfuric acid was added to the solution.

in sulfuric acid is equal to −0.642 volt. The large difference between the values of the potentials makes it comparatively simple to separate indium and cadmium completely in sulfuric acid solution by means of a zinc amalgam. The results obtained are shown in the diagram.




Separation of In and Cd by means of a zinc amalgam: 1,2) For indium; 3,4) for cadmium (curves 2 and 4 are enlarged 25 times along the ordinate).

Elements such as As, Sb, Bi, Cu, Tl, Se, Sn, Ma, Ti, Fe(III) and some others are vigorously reduced by the zinc amalgam. Under such conditions, some (Cd, Sn, Tl, and Cu) dissolve in the mercury, while others (As, Sb, Bi, Se, and Te) are deposited in the elemental state in the form of an insoluble, friable, deposit. Elements with higher valency are reduced to lower valency states ($Fe^{III}$, $V^{V}$, $Cr^{VI}$, and $Ti^{IV}$).

The technique developed has been checked on various samples of indium raw material.

The analytical procedure adopted for the polarographic determination of indium by the amalgam method is as follows. An aliquot of test material (1-3 g) is decomposed on heating in a mixture of nitric and sulfuric acid until the sample has been broken down completely, and until copious white fumes appear. After cooling, the sample is treated with hot water, and, in the event of the presence of an appreciable amount of precipitate in the solution, the latter is allowed to stand and then filtered. To the solutions thus obtained is added sulfuric acid (or an equivalent amount of some suitable sulfate), so that its final concentration is not less than 20%; the solution is then cemented with zinc amalgam* at room temperature. The zinc amalgam is prepared by dissolving zinc metal in mercury on heating in the presence of dilute sulfuric acid. Treatment of the solution with the amalgam, for a stirrer rate of 350-400 revolutions/minute, takes about 45 minutes. When cementation is complete, the solution is filtered, if necessary, and then about 10% of its weight of a soluble chloride (for example NaCl) added to it; indium is then determined in this solution polarographically.

*When sulfates are used it is essential to add some $H_2SO_4$ in order to avoid hydrolysis.

TABLE 2

Results for the Quantitative Determination of Indium in Various Types of Indium-Containing Raw Material

| Firms supplying test material / Elements in % | Bi | Zn | Al | As | Fe | Pb | Sb | Cd | Cu | Sn | Indium content as found by the following methods: spectro. | Aref'eva | amalgam |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ChETsZ | 0,1 | 20,0 | 10,0 | 0,05 | 0,5 | 0,3 | 0,05 | 0,02 | 0,05 | 0,01 | 5 | 5,00 | 5,01<br>5,00<br>5,00 |
| KMZ | 15,0 | 25,0 | — | 2,3 | 8,0 | 0,04 | 0,10 | 1,5 | 1,6 | 0,14 | 0,4 | 0,40 | 0,39<br>0,40<br>0,40 |
| Ukrtsink | 0,1 | 21,2 | 4,7 | 0,5 | 2,4 | 10,0 | — | 0,58 | 0,68 | — | 0,04 | 0,04 | 0,04<br>0,04<br>0,042 |


## SUMMARY

A new method has been developed for removing interfering elements prior to polarographic determination of indium in concentrates and in processed materials. The method consists of treating sulfuric acid indium solutions containing 20% free sulfuric acid (or the equivalent amount of other sulfates) with a zinc amalgam; the chloride of an alkali metal is then added to the solution purified in this way, the amount of chloride added being sufficient to bring its concentration up to 10% (with respect to the weight of the solution); indium is then determined polarographically.


## LITERATURE CITED


[1] A. M. Bronshtein, Information No. 194, TsIIN, Ministry of Nonferrous Metallurgy, USSR, 1956, p. 159.*

[2] N. F. Zakhariya and Ta. A. Leiderman, Information No. 194, TsIIN, Ministry of Nonferrous Metallurgy USSR, Moscow, 1956, p. 163.

[3] A. K. Rusanov, Improved Spectrographic Method for the Determination of Rare Metals. From a Report given at the All-Union Conference on Rare and Dispersed Metals. Leningrad, June 1957 [in Russian].

[4] B. S. Tsybina and T. V. Vladimirova, Information No. 194, TsIIN, Ministry of Nonferrous Metallurgy USSR, Moscow, 1956, p. 130.

[5] B. S. Tsybina and N. K. Davidovich, Information No. 194, TsIIN, Ministry of Nonferrous Metallurgy USSR, Moscow, 1956, p. 126.

[6] A. I. Busev, "Methods of Analyzing Rare and Non-Ferrous Metals," Collection of Articles, Izd MGU, 1956, p. 79 [in Russian].

[6a] A. I. Busev , "The Analytical Chemistry of Indium," [in Russian], Moscow, Izd AN SSSR, 1958.

[7] T. F. Aref'eva, A. A. Pozdnyakova, and R. G. Pats, Collection " Enrichment and Metallurgy of Non-Ferrous Metals," [in Russian], Metallurgizdat, Moscow, 1953, p. 125.

[8] P. A. Gurin, Bulletin VIMS 11, 1955; a report given at the All-Union Conference on Rare and Dispersed Metals, Leningrad, June 1957 [in Russian].

[9] S. I. Sinyakova, Proc. Acad. Sci. 29, 375, (1940).

[10] G. Semerano, Atti Accadem. nazl. Rend. classe Sci. fis. mat. nat. 6, 556 (1949); cited in Chem. Abstrs. 45, 10124 (1951).


*In Russian.

[11] R. Bock, H. Kusche, and E. Bock, Z. analyt. Chem. 138, 167 (1953).

[12] N. V. Akselrud and V. B. Spivakovskii, J. Anal. Chem. 12, 79 (1956).*

[13] A. T. Nizhnik, Trans. Chem. Inst. of the Academy of Sciences of the Ukrainian SSR 9, 103 (1947).

[14] I. M. Kolthoff and D. D. Lingane, "Polarography," [Translated from English], ONTI, Moscow-Leningrad, 1948, p. 268.

[15] A. K. Babko, A. B. Polishchuk, and A. I. Volkova, Trans. Chem. Inst. of the Academy of Sciences of the Ukrainian SSR, 7, 505 (1941).

[16] S. P. Bukhman, "Cementation by Amalgams as a Method for the Separation and Isolation of Certain Rare Metals," Thesis, Alma-Ata, 1954.

[17] R. J. Seward, J. Amer. Chem. Soc. 55, 2740 (1953).

[18] F. Ensslin, Z. anorg. Chem. 254, 83 (1947).

[19] I. D. Muzyka, J. Gen. Chem. 23, 918 (1953).*

[20] N. V. Aksel'rud, Ukrainian Chem. J. 21, 457 (1955).

Received July 24, 1957

*Original Russian pagination. See C.B. Translation.

# INCREASING THE SENSITIVITY AND ACCURACY OF THE DETERMINATION OF CESIUM IN MINERALS BY THE FLAME-PHOTOMETRIC METHOD

E. A. Fabrikova

Institute of Mineralogy, Geochemistry, and Crystallochemistry of Rare Elements, Acad. Sci. USSR, Moscow

Determination of cesium in natural raw material requires highly sensitive methods, since this element is found, for the most part, in trace amounts.

The sensitivity and accuracy of the determination of cesium and other elements by flame photometry, depends not only on the refinements of the spectroscopic and electronic apparatus, but also on the techniques adopted for measurement. We have developed a flame photometric method of determining cesium, which permits hundredths and thousandths of a percent of this element to be determined in natural materials with an accuracy of 5-10%. The minimum amount of cesium (0.2 $\gamma$/ml) which can be determined by the suggested method is one and a half times that which can be determined by Horstman's method [1] which is applicable to the determination of cesium in silicates. The increased sensitivity is achieved by making use of the effect in which the intensity of the cesium radiation ($\lambda$ = 8521 A) is enhanced in the presence of large amounts of potassium.

Using a flame photometric method, a study was made of the effect of the alkali elements (K, Na, Li, and Rb) present as impurities, on the intensity of the radiation of Cs at $\lambda$ = 8521 A.

The test solution of cesium sulfate (0.56, 2.8, and 30$\gamma$ Cs/ml) containing appropriate additions of potassium, sodium, lithium, and rubidium was introduced into an acetylene-air flame by means of a needle sprayer with a glass compartment. The spectrum line analyzer used was a UM-2 monochromator covering the spectral range 3800-10,000 A and with a linear dispersion in the red range of 335 A/mm. The radiation intensity was determined by means of a FEU-22 photomultiplier (integral sensitivity 30a/lumen) and a mirror galvanometer type M-21 ($1.5 \times 10^9$ a/mm). The sensitivity was regulated by means of a 10,000 ohm resistance box connected in parallel with the galvanometer. The operating slit width of the monochromator was 0.1 mm.

During measurements of the radiation intensity of cesium, corrections were made for the background of the burner flame and the characteristic radiation of the additives.

It has been established that the presence of alkali metals in the test solution leads to an appreciable increase in the intensity of the cesium radiation ($\lambda$ = 8521 A), when the concentration of the impurity is higher than the cesium concentration. Potassium shows the greatest effect. The curves relating the intensity of the Cs radiation and the potassium concentration of the solution indicate a saturation character (Fig. 1). At potassium concentrations corresponding to the saturation points, the intensity of the cesium radiation increases up to 25 times. The standard curve relating the intensity of the Cs radiation ($\lambda$ = 8521 A) to cesium concentration (0.2-100 $\gamma$/ml), and taken in the presence of large amounts of potassium — 2500 $\gamma$/ml (5570 $\gamma$/ml $K_2SO_4$) - is almost linear; this same curve has a break when pure cesium salt is used (i.e., when no potassium is present) (Fig. 2). It is important to note then, when the test solution is "saturated" with potassium, the effect of additions of Na, Li, and also of Rb is not perceptible, as long as the amounts of these other elements are of the same order as that of cesium.

In essence, the method which has been developed reduces to the addition of large amounts of potassium sulfate (5570 γ/ ml) to both the test solution and standard solutions prior to carrying out flame-photometric measurements. The correction to be applied for the background arising from the characteristic radiation of the potassium introduced, is established by measuring the emission of a pure solution of potassium sulfate (5570 γ/ ml)

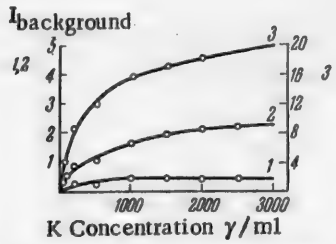



Fig. 1. Effect of potassium on the spectral emission of cesium (λ = 8521 A ). Cs content: 1) 0.5 γ/ml; 2) 2.8 γ/ml; 3) 30 γ/ml; $I_{background}$, the current in scale divisions of the galvanometer.

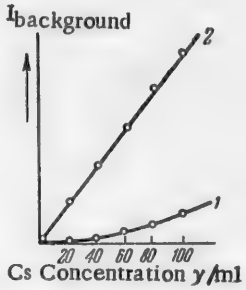



Fig. 2. Standard cesium curves. Potassium content: 1) 0; 2) 2500 γ/ ml; $I_{background}$, the current in scale divisions of the galvanometer.

when the monochromator is set at the cesium wave length (8521 A). Potassium is added to the test solution in amounts which take into account the amount of potassium already present in the original material, the original potassium content being measured with an accuracy of 50 γ /ml. The value for the original potassium contents of the test solutions are determined beforehand by flame photometric determination of potassium ( λ = 7665, 7699 A) using a standard curve.

Test samples are chemically prepared by Ellestad and Horstman's method [2]. The sample is broken down by means of hydrofluoric and sulfuric acids, and then precipitation carried out using basic lead carbonate. After such a treatment, the solution which is to be analyzed for cesium contains the other alkali metals (Na, K, Li, and Rb) and Mg as well as the cesium. The flame-photometric method proposed, in which potassium is added, prevents interference from the remaining impurities.

The accuracy of the method was checked by determination of cesium in a silicate sample, before and after addition of a known amount of cesium (Table 1). The mean relative error during determination of hundredths of a percent of cesium amounts to ±4.45%; during determination of thousandths of a percent of cesium the error is ±9.7%. The reproducibility of the method was checked by replicate determinations of the same amount of cesium using various calibration curves (Table 2).

Experimental procedure. 0.5-1 g of sample contained in a platinum basin is moistened with water, and 0.4 ml of concentrated $H_2SO_4$, 20 ml of HF, and 2-3 drops of $HNO_3$ added. The mixture is heated to 70-80°. As decomposition proceeds the heating is increased and is finished when white fumes appear. The residue is cooled and 2 ml of water added, this is followed by 0.1 ml of concentrated sulfuric acid and the whole heated again until white fumes appear. In order to make sure that all fluorides have been broken down, the residue is heated again after addition of 5 ml of water. 25-30 ml of water is added to the final residue and the whole heated to dissolve the salts. The liquid is transferred to a 150 ml beaker and diluted to 70 ml. The solution obtained is heated until it starts to boil gently when powdered basic lead carbonate is added to it with stirring until the liquid gives an alkaline reaction to methyl red. Solution and precipitate are boiled for several minutes, the mixture is stirred carefully and filtered through an 11 cm (white band). The precipitate is washed with hot water until the combined volume of filtrate plus washings is 120-130 ml. This solution is concentrated to a volume of 30 ml, cooled, and then filtered through a small funnel into a 50 ml standard flask; the volume is made up to the mark with water, the solution thus obtained is then the original solution to be used for the photometric measurements.

Flame-photometric measurements start with a preliminary determination of the potassium content (7665-7699 A) of this original solution, using calibration curves constructed with the aid of standard potassium solutions.

In order to determine the cesium content, an aliquot of the original solution (20 ml) is mixed in a 25 ml standard flask with a potassium sulfate solution (0.557 g/ml of $K_2SO_4$ or 25000 γ/ml of K) so that, after dilution of the solution to give a concentration suitable for cesium determination, it contains 2500 γ/ml of K.

TABLE 1

Determination of Cesium in Rocks

| Rock | Content, in % | | | Cesium, in % | | Relative error, in % |
|---|---|---|---|---|---|---|
| | Na | K | Li | added | found* | |
| Biotite granite | 4,1 | 5,8 | 0,011 | 0,012 | 0,011 | — 8,3 |
| Vein-granite | 5,4 | 5,8 | 0,007 | 0,029 | 0,031 | + 6,9 |
| » | 5,4 | 5,8 | 0,007 | 0,033 | 0,037 | +12,1 |
| Muscovite granite | 3,3 | 5,7 | 0,003 | 0,055 | 0,056 | + 1,8 |
| » | 3,3 | 5,7 | 0,003 | 0,096 | 0,099 | + 3,1 |
| Duplo-micaceous granite | 3,7 | 5,0 | 0,017 | 0,184 | 0,184 | 0 |
| » | 3,7 | 5,0 | 0,017 | 0,148 | 0,150 | + 1,3 |
| » | 5,0 | 6,0 | 0,013 | 0,085 | 0,080 | — 5,9 |
| » | 5,0 | 6,0 | 0,013 | 0,101 | 0,104 | + 3,0 |
| Muscovite granite | 3,3 | 6,3 | 0,013 | 0,077 | 0,073 | — 5,2 |
| » | 3,3 | 6,3 | 0,013 | 0,063 | 0,064 | + 1,6 |
| Duplo-micaceous granite | 2,9 | 5,4 | 0,002 | 0,0018 | 0,0016 | —11,1 |
| » | 2,9 | 5,4 | 0,002 | 0,0035 | 0,0032 | — 8,6 |
| » | 2,9 | 5,4 | 0,002 | 0,0062 | 0,0056 | — 9,6 |

*Cesium was absent in the samples of natural silicates indicated.

The volume of potassium solution to be added is calculated by means of the formula:

$$V = \frac{2500 \cdot 25 - C_K \cdot 20}{25000},$$

where $C_K$ is the concentration of potassium in the original solution in γ/ml. Using this formula, it is possible to compile a table for the volume of potassium salt solution to add, as a function of the potassium content of the test solution, within the limits 50- 2500 γ ml.

After addition of the requisite amount of potassium, the test solution is diluted to 25 ml and this solution then used for photometric determination of cesium ( λ = 8521 A). At the same time as the test solution is being measured flame-photometrically, a standard solution of cesium sulfate to which $K_2SO_4$ has been added in an amount corresponding to 2500 γ/ml of K, and a standard solution of potassium sulfate containing 2500 γ/ml of K, are also measured photometrically under the same conditions.

TABLE 2

Reproducibility of Cesium Determinations in the Presence of 2500 γ of Potassium /ml

| Series No. | Cs found in γ/ml | | | | | | | | | | Mean error, in % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0,17 | 0,17 | 0,19 | 0,20 | 0,15 | 0,21 | 0,16 | 0,17 | 0,20 | 0,18 | 8,8 |
| 2 | 2,0 | 1,9 | 2,0 | 1,9 | 1,9 | 2,2 | 1,9 | 2,1 | 2,1 | 2,0 | 4,0 |
| 3 | 18,2 | 18,3 | 18,1 | 18,2 | 17,4 | 18,5 | 18,3 | 19,1 | 18,7 | 18,4 | 1,5 |

The cesium content of the test material is calculated by means of the formula:

$$\%Cs = \frac{C_{st}\,(I_x - I_K)\;25 \cdot 50 \cdot 100}{(I_{st} - I_K)\,Q \cdot 10^6 \cdot 20},$$

where $C_{St}$ is the Cs concentration of the standard solution; $I_{St}$ is the deflection of the galvanometer needle during measurement of the standard cesium solution; $I_x$ ditto for the test solution; $I_K$ ditto for the potassium sulfate solution; Q weight of sample in g dissolved in the original volume.

A standard solution of cesium sulfate is prepared by dissolving 1 g of CsCl in water in a 50 ml platinum basin. To this solution is added 2 ml of 4 N $H_2SO_4$. The contents of the basin are evaporated to dryness. The sulfate thus obtained is brought to constant weight by calcining at a weak-red heat. The salt is dissolved in distilled water in a 500 ml flask and the volume made up to the mark. The exact content of cesium in per ml of the solution obtained is calculated from the weight of the sulfate. Working solutions are prepared by dilution of this stock solution, and addition of 2500 γ/ml K. The number of working solutions depends on the range of concentrations to be measured. Thus for cesium concentrations within the range 0.2-100 γ/ml Cs we used three standards: 1 γ/ml Cs + 2500 γ/ml K; 20 γ/ml Cs + 2500 γ/ml K; and 80 γ/ml Cs + 2500 γ/ml K.

The potassium sulfate solution containing 25,000 γ/ml K was prepared from the recrystallized sulfate which had been dried at 100°. 27.85 g $K_2SO_4$ is dissolved in 500 ml water.

The method which has been tested out on more than 300 samples of various natural silicates, has been adopted at the Chemico-Analytical Section of the Institute of Mineralogy, Geochemistry, and Crystallochemistry of the Rare Elements, Acad. Sci. USSR.

## SUMMARY

A highly sensitive method has been developed for the determination of cesium in minerals by flame photometry. This method is based on the enhanced intensity of the cesium radiation obtained on addition of large amounts of potassium to the test solution.

## LITERATURE CITED

[1] E. L. Horstman, Analyt. Chem. 28 1417 (1956).

[2] R. B. Ellestad and E. L. Horstman, Analyt. Chem. 27, 1299 (1955).

Received November 28, 1957

# SPECTROCHEMICAL DETERMINATION OF MAGNESIUM AND THE EFFECT OF THE MAGNESIUM CONTENT ON THE ANALYSIS OF SILICON AND MANGANESE IN CAST IRON

A. S. Dem'yanchuk and E. D. Kukharenko

E. O. Paton Institute of Welding and the Institute of Machinery, Acad. Sci. Ukrainian SSR, Kiev

Cast iron usually contains 0.03-0.12% of Mg; magnesium is mainly found in the form of compounds (MgS, MgO, $Mg_2S$, etc.) [1]. Determination of magnesium by chemical methods is fairly complicated and is not accurate enough. The use of a spectrographic method in the given instance has led to a successful solution of this problem [2-3]. Development of a technique for the determination of magnesium in cast iron, using a high-frequency spark as a spectrum-excitation source, seemed to us to be of considerable practical interest [4].

The work was carried out on a "Hilger" average dispersion spectrograph, using conditions which have been described earlier [5]. The fixed electrode used was made from copper.

A cylindrical profile with a flatly sharpened operating part 1.6 mm in diameter was chosen for sharpening the fixed electrode. This form of sharpening makes it possible, after each cleaning, to control the dimensions of the working part of the fixed electrode, and, moreover, favors treatment of the surface of the test samples by the discharge.

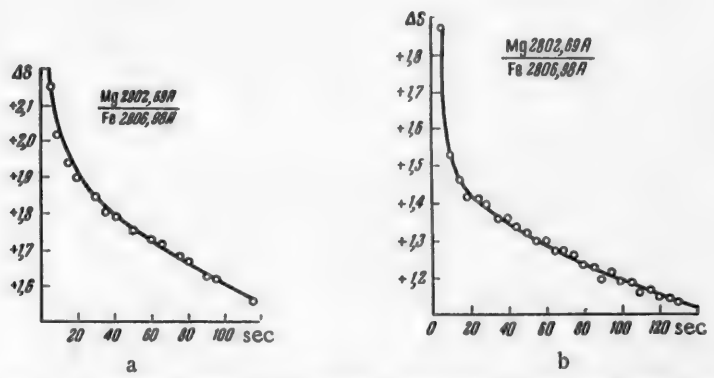



Fig. 1. Sparking curves for different magnesium contents of the cast: a) 0.12% Mg; b) 0.068% Mg.

Magnesium, which is very active chemically, interacts with individual elements, and is also readily oxidized by atmospheric oxygen. Under the action of a spark discharge incomplete burning of the magnesium from the surface layer of the sample occurs; the sparking curves testify to this (Fig. 1, a and b). Comparison of these curves, constructed for different magnesium contents of the cast, shows that after 30 seconds, there occurs some stabilization of the relative intensity of the analytical pair of lines Mg 2802.69 — Fe 2806.98 A (the slope of the lines is preserved almost the same). Accordingly, we chose a preliminary sparking time of 30 seconds. The exposure time was 20 seconds.

In Fig. 2 is shown a typical calibration curve for the determination of magnesium in cast; this curve was constructed on the basis of 15 standards prepared from production samples and carefully analyzed in several chemical laboratories.

Curves obtained with a high-frequency spark are characterized by high values for the slope. The technique suggested is distinguished by good reproducibility of the results obtained, and a completely satisfactory accuracy.

Under chosen conditions it is possible, on the basis of one photograph of the spectrum, to determine magnesium, manganese, and silicon in cast, as a result of which the time taken for determination of the element indicated in cast is considerably reduced.

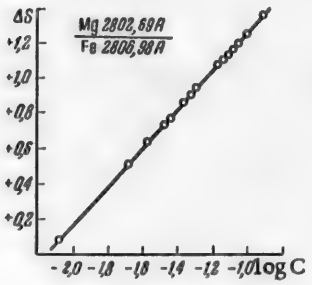



Fig. 2. Calibration curve for the determination of magnesium in cast. Spectrum excitation source—high-frequency spark.

Similar conditions were also found for a high-voltage condensed spark. The spectra were photographed under the following conditions: an IG generator, complex scheme; capacity 0.01 microfarad; induction 0.01 millihenries; analytical gap 2 mm; upper electrode—copper; sparking—60 seconds; exposure time —45 seconds. The photographic plates were spectrographic type 1.

The following pairs of analytical lines were used for the high-frequency spark method, and for the high-voltage method, for determination of magnesium, manganese, and silicon in cast;

Mg 2802.69 — Fe 2806.98 A, Mn 2933.1 — Fe 2926.6 A
and Si 2881.6 — Fe 2880.7 A.

We studied the effect of the magnesium content of the cast on the determination of silicon and manganese, using the spectrum excitation sources indicated. Table 1 contains results obtained during the analysis of silicon and manganese in cast before and after addition of magnesium. As these results show, the magnesium content has no effect on the results of the spectrochemical determination of silicon and manganese.

For studying the effect of the magnesium content on the analytical results for silicon and manganese in cast, by means of an a.c. arc, production samples were used. The spectra were photographed on an ISP-22 spectrograph under the following conditions: spectrum excitation source— an a.c. arc PS-39, current 4 amps; analytical gap 2 mm; slit width of the spectrograph—0.015 mm; arcing —10 seconds; exposure time —15 seconds; upper electrode—a copper rod sharpened to a cone with a flat of 2-2.5 mm. The photographic plates were spectrographic type 1. For determination of magnesium, manganese, and silicon in cast, the following analytical lines were used: Mg 2802.69—Fe 2806.98 A, Mn 2939.30—Fe 2926.59 A and Si 2519.21—Fe 2518.10 A.

TABLE 1

| Melt no. | Content of the element, in % | | | | | | Mg |
|---|---|---|---|---|---|---|---|
| | IG-2 | | high-frequency spark | | chemical composition | | |
| | Si | Mn | Si | Mn | Si | Mn | |
| 313 original | 3,71 | 0,56 | 3,65 | 0,57 | 3,67 | 0,55 | — |
| 313 with magnesium | 3,64 | 0,56 | 3,66 | 0,56 | 3,64 | 0,53 | 0,098 |
| 400 original | 3,52 | 0,58 | 3,54 | 0,60 | 3,55 | 0,59 | — |
| 400 wigh magnesium | 3,48 | 0,59 | 3,50 | 0,58 | 3,49 | 0,57 | 0,108 |
| 400 original | 3,64 | 0,61 | 3,61 | 0,62 | 3,62 | 0,63 | — |
| 403 with magnesium | 3,55 | 0,63 | 3,59 | 0,59 | 3,57 | 0,60 | 0,098 |
| 418 original | 3,73 | 0,69 | 3,70 | 0,68 | 3,75 | 0,70 | — |
| 418 with magnesium | 3,69 | 0,68 | 3,71 | 0,67 | 3,71 | 0,69 | 0,162 |

In order to study the effect of magnesium on the relative intensities of the lines for silicon and manganese in cast, sparking curves were constructed for these elements (Fig. 3, a,b). A comparison of these curves

shows that the relative intensity of the silicon and manganese lines increases appreciably for casts with high magnesium contents as compared with the original casts (for the same amounts of silicon and manganese in these casts). Casts with different magnesium contents were examined (Table 2).

The results obtained make it possible to assess the difference in the effect of magnesium on the absolute and relative intensity of the silicon and manganese lines; it is dependent, in the first instance, on the amount of magnesium in the cast iron.

For magnesium contents in the cast up to 0.04%, the absolute intensities of the silicon and manganese lines, and of the comparison lines are somewhat lower than the absolute intensities of the lines of these same elements in the original cast. But, since the corresponding relative intensities of the test lines of the magnesium cast and the original cast are very similar in value, the effect of magnesium of the final analytical results is almost excluded.

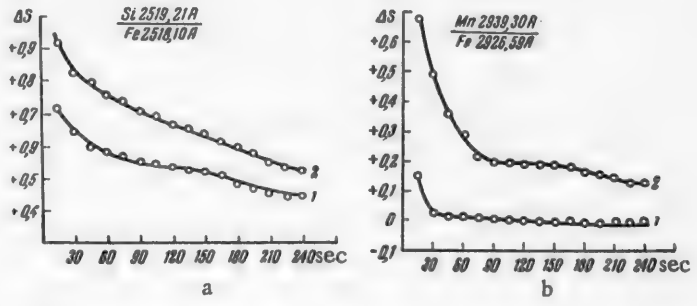



Fig. 3. Sparking curves for silicon (a) and manganese (b); 1) Original cast; 2) cast to which magnesium has been added (0.12% Mg) Spectrum excitation source—a PS-39 arc generator.

It is evident from Table 2 that for magnesium contents, for example, of 0.011%, the results for silicon and manganese in the original and in the magnesium cast, are almost identical and correspond to the true values; this was confirmed by chemical analysis.

At higher magnesium contents of the cast—up to 0.06%— the absolute and relative intensities of the silicon and manganese lines are somewhat higher than one would expect.

TABLE 2

| Sample | $S_{Si}$ | $S_{Fe}$ | ΔS | $S_{Mn}$ | $S_{Fe}$ | ΔS | Content, in % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Si | Mn | Mg |
| Melt 299 — original cast | 64,0 | 113,2 | −49,2 | 64,7 | 132,0 | −67,3 | 0,60 | 0,27 | — |
| Melt 299 — cast plus magnesium | 61,9 | 111,2 | −49,3 | 60,7 | 130,0 | −69,3 | 0,60 | 0,26 | 0,011 |
| Melt 406 — original cast | 169,8 | 109,1 | +60,7 | 124,0 | 119,5 | + 4,5 | 3,51 | 0,66 | — |
| Melt 406 — cast plus magnesium | 167,1 | 106,7 | +60,4 | 119,5 | 115,2 | + 4,2 | 3,48 | 0,65 | 0,024 |
| Melt 427 — original cast | 121,1 | 89,8 | +31,3 | 110,0 | 100,0 | +10,0 | 1,70 | 0,72 | — |
| Melt 427 — cast plus magnesium | 120,5 | 88,9 | +31,6 | 109,5 | 100,0 | + 9,5 | 1,73 | 0,71 | 0,033 |
| Melt 303 — original cast | 117,9 | 80,0 | +37,9 | 75,3 | 101,0 | −25,7 | 2,02 | 0,36 | — |
| Melt 303 — cast plus magnesium | 120,1 | 76,4 | +43,7 | 81,5 | 97,5 | −16,0 | 2,37 | 0,43 | 0,045 |

The effect of the magnesium content of the cast on the intensity of the silicon and manganese lines is most clearly demonstrated at magnesium contents higher than 0.06% (Table 3).

The results given in Table 3 show that the relative intensity of the lines in samples of the original cast and in cast containing magnesium, with approximately equal amounts of silicon and manganese, differs essentially. The intensity of the silicon and manganese lines in cast containing magnesium is appreciably higher than that of the lines in the original cast; this is a consequence of the effect of magnesium. Results for the spectrographic determination of silicon and manganese in magnesium cast are one and a half to twice the true content of these elements in the metal.

Many examples are given in the literature of the effect of the third component on the results of the determinations of a number of elements [6, 7, 8].

On the basis of the experiments described above it is clear that with increasing magnesium content, which affects the fusion temperature of the melt, the intensity of the analytical lines of silicon and manganese

TABLE 3

| Sample | $S_{Si}$ | $S_{Fe}$ | $\Delta S$ | $S_{Mn}$ | $S_{Fe}$ | $\Delta S$ | Content, in % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Si | Mn | Mg |
| Melt 312 – original cast | 170,0 | 104,0 | +66,0 | 132,8 | 127,0 | + 5,8 | 3,94 | 0,62 | — |
| Melt 312 – cast plus magnesium | 180,0 | 93,0 | +84,0 | 146,8 | 110,0 | +46,8 | 6,38 | 1,22 | 0,118 |
| Melt 313 – original cast | 169,3 | 105,0 | +64,3 | 121,0 | 122,0 | — 1,0 | 3,76 | 0,55 | — |
| Melt 313 – cast plus magnesium | 183,0 | 103,0 | +80,0 | 145,1 | 105,0 | +40,1 | 5,75 | 1,09 | 0,098 |
| Melt 409 – original cast | 171,3 | 105,0 | +66,3 | — | — | — | 3,55 | — | — |
| Melt 409 – cast plus magnesium | 180,0 | 95,0 | +85,0 | — | — | — | 5,62 | — | 0,068 |
| Melt 400 – original cast | 172,0 | 110,8 | +61,2 | 154,0 | 150,5 | + 3,5 | 3,55 | 0,62 | — |
| Melt 400 – cast plus magnesium | 187,0 | 105,0 | +82,0 | 176,0 | 129,0 | +47,0 | 6,69 | 1,17 | 0,108 |
| Melt 403 – original cast | 172,0 | 110,0 | +62,0 | 152,0 | 147,0 | + 5,0 | 3,63 | 0,64 | — |
| Melt 403 – cast plus magnesium | 185,0 | 102,5 | +82,5 | 185,0 | 134,0 | +51,0 | 5,75 | 1,29 | 0,098 |
| Melt 418 – original cast | 162,0 | 102,0 | +60,9 | 114,5 | 110,0 | + 4,5 | 3,76 | 0,73 | — |
| Melt 418 – cast plus magnesium | 172,0 | 98,0 | +74,0 | 138,0 | 100,0 | +38,0 | 5,50 | 1,12 | 0,163 |
| Melt 420 – original cast | 167,1 | 102,0 | +65,1 | 135,0 | 131,0 | + 4,0 | 3,89 | 0,60 | — |
| Melt 420 – cast plus magnesium | 176,5 | 93,0 | +83,5 | 154,0 | 108,0 | +46,0 | 6,31 | 1,12 | 0,160 |

increases when an arc discharge is used. This leads to the conclusion that magnesium affects the evaporation process of these elements in the arc, and, consequently, affects the experimental results. Similar phenomena have been observed during the analysis of copper alloys, [9], and, to a smaller extent, during the analysis of aluminum alloys [10].

## SUMMARY

1. A technique has been developed for the spectrographic determination of magnesium in modified cast iron using a high-frequency spark as a spectrum excitation source. The technique permits determination of 0.005%, and more, of magnesium.

2. It has been established that the intensity of the spectral lines of silicon and manganese in cast depends to a considerable extent on the magnesium content of the cast when an arc discharge is used. The intensity of the lines of these elements increases appreciably with increasing magnesium content. For magnesium contents of the cast in excess of 0.06%, the amount of the silicon and manganese as determined spectrographically is one and a half to a twice as much as the true content of these elements in the metal.

3. Magnesium does not affect the results obtained during spectrographic determination of Si and Mn in casts, when a condensed spark generator and a high-frequency spark are used.

## LITERATURE CITED


[1] K. I. Vashchenko and L. Sofroni, "Magnesium Cast", [in Russian], Mashgiz, 1957, Kiev—Moscow.

[2] A. S. Komarovskii, Industrial Labs. 16, 1132 (1950).

[3] L. L. Mirkin and É. P. Rikman, Industrial Labs. 22, 930 (1956).

[4] E. S. Kudelya, "Spectrographic Analysis of Welded Seams", Institute of Electric Welding Press, Acad. Sci. Ukrainian SSR, 1951, Kiev.

[5] E. S. Kudelya and A. S. Dem'yanchuk, Industrial Labs. 20 (1954).

[6] N. M. Gegechkori, T. B. Edneral, and S. L. Mandel'shtam, Industrial Labs. 12, 559 (1946).

[7] V. G. Koritskii, Bull. Acad. Sci. USSR, Phys. Ser. 9, 647 (1945).

[8] G. E. Panchenko, Bull. Acad. Sci. USSR. Phys. Ser. 5, 313 (1941).

[9] V. K. Prokof'ev, Bull. Acad. Sci. USSR, Phys. Ser. 11, 289 (1947).

[10] N. A. Rudnevskii, Bull. Acad. Sci. USSR, Phys. Ser. 14, 642 (1950).



Received November 25, 1957

# PHOTOMETRIC DETERMINATION OF TOTAL RARE EARTHS IN ORES AND ROCKS

F. V. Zaikovskii and V. S. Bashmakova

All-Union Institute of Mineral Raw Materials, Moscow

Tha aim of our investigation was to develop a photometric method for determining from 0.01 to 2-3% of total rare earths (T.R.E) in ores and rocks. The work is a continuation of work published earlier [1, 2] on the use of arsenazo I [3] and the method of developing reagents [2].

The chlorides of the rare earths of the cerium (T.R.E. -Ce) and yttrium groups (T.R.E. -Y) were used in this work. Total rare earths were extracted from the minerals by the usual oxalate method. Their chemical composition was (in %): T.R.E. -Ce — $Ce_2O_3$ 41.0; $La_2O_3$ 13.3; $Pr_2O_3$ 5.5; $Nd_2O_3$ 23.0; $Sm_2O_3$ 5.0, etc., T.R.E. - Y($Y_2O_3$, $Er_2O_3$) 58.0, etc.

1% Solutions of the chlorides of the T.R.E. and the content of the T.R.E. in these solutions was established gravimetrically after precipitation with ammonia. The working solution was prepared from the 1% solution of T.R.E. containing 30γ T.R.E./ml and had a pH of 3.

TABLE 1

Optical Density of Solutions of the Complexes of the Metals with Arsenazo in the Presence (I), and in the Absence (II) of Sulfosalicylic Acid

| Metal oxide, 30γ/25 ml | Optical density | | Equivalent to T.R.E. | | Difference in γ of T.R.E. | |
|---|---|---|---|---|---|---|
| | (I) | (II) | (I) | (II) | (I) | (II) |
| T.R.E. - Ce | 0,21 | 0,20 | 30,0 | 30,0 | — | — |
| T.R.E. - Y | 0,22 | 0,21 | 30,0 | 30,0 | — | — |
| $Y_2O_3$ | 0,30 | 0,32 | 42,0 | 48,5 | +12,0 | +18,5 |
| $Ce_2O_3$ | 0,24 | 0,22 | 32,5 | 31,0 | + 2,5 | + 1,0 |
| $La_2O_3$ | 0,20 | 0,22 | 28,5 | 35,0 | — 1,5 | + 5,0 |
| $ThO_2$ | 0,18 | 0,09 | 25,0 | 14,0 | — 5,0 | —16,0 |
| $ZrO_2$ | 0,01 | 0,01 | 1,5 | 1,5 | —28,5 | —28,5 |
| $TiO_2$ | 0,02 | 0,06 | 2,5 | 8,0 | —27,5 | —22,0 |
| $Al_2O_3$ | 0,00 | 0,27 | 0,00 | 41,0 | 0,00 | +11,0 |

The solutions used for studying the optical properties of the complexes of the metals with arsenazo were prepared as follows. Into a 25 ml standard flask was introduced a solution containing the metal ion (equivalent to 30 γ of the metal oxide), 0.5 ml of 10% sulfosalicylic acid, 3 ml of 0.05% arsenazo solution, and 4 ml of a 20% solution of urotropine, and the whole made up to the mark with water and mixed; the pH of such a solution was 6.7-6.8. The reference solution was prepared in the same way but with omission of the metal salt.

The optical density of the solutions (Table 1) was measured on a FEK-M photocolorimeter, using 30 mm cells and a yellow-green filter ( λ 570 mμ).

Equimolar amounts of the elements of the cerium and yttrium groups give solutions with almost equal optical density with arsenazo. Increasing the yttrium content of the T.R.E. will increase the optical density since yttrium taken individually increases the optical density in comparison with cerium and lanthanum. As can be seen from Table 1, in the presence of sulfosalicylic acid, titanium (IV) and zirconium have almost no effect on the optical density, while thorium increases it.

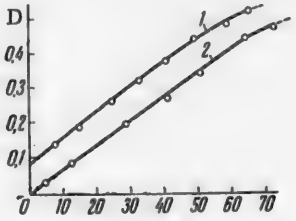



Fig. 1. Optical density of the complexes of the rare earths with arsenazo in the presence of 1.5 mg of calcium (Curve 1) and in the absence of calcium (Curve 2).

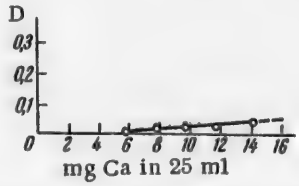



Fig. 2. Optical density of the complex of calcium with arsenazo in the presence of 50 mg sulfosalicylic acid.

In neutral media, calcium forms a complex with blue-violet color with arsenazo. Calcium is often met in large quantities in ores, and is also used as a precipitant in the oxalate method. In Fig. 1, is shown the optical density of the complexes of the T.R.E. with arsenazo in the presence of 1.5 mg of calcium (Curve 1), and in the absence of calcium (Curve 2). Calcium sulfosalicylate is colorless, it does not give a color with arsenazo. In Fig. 2, is shown the optical density of the complex of calcium with arsenazo in the presence of 50 mg of sulfosalicylic acid per 25 ml solution. In the presence of sulfosalicylic acid, as can be seen from Fig. 2, no color resulting from the complex develops at calcium contents up to 6 mg; greater amounts of calcium increase the optical density of the solution significantly.

Separation of thorium from the rare earths. Thoron [4], arsenazo [3], pyrocatechol violet [5], hydroxyhydroquinone rose [6], quinalizarin [7], and Schiff Base,* and many other compounds form finely dispersed deposits, in the form of a suspension, with thorium. Separation of the suspension from the aqueous phase by the use of fine-pore filters is not possible, but activated charcoal readily adsorbs the thorium complex and also the reagent.

To 30 ml of solution containing 218 γ thorium and 215 γ T.R.E., at the pH shown in Table 2 to be the optimum for color development, was added 2 ml of a 0.1% aqueous (alcoholic for quinalizarin and the Schiff Base) solution of the reagent in a large excess. On mixing, a color characteristic of the given complex developed. After 2-3 minutes, 0.1 g of activated charcoal was added to the solution and the whole shaken up, and then filtered through a "white band" filter 9 cm in diameter.

Thorium was determined in the solution and in the adsorbent (after burning off the carbon) by a method described in one of our papers [1], while the T.R.E. was determined as described above.

It is clear from Table 2 that pyrocatechol violet, hydroxyhydroquinone rose, and quinalizarin do not permit separation of thorium and T.R.E. since the T.R.E. are adsorbed from the solution as well as thorium. Using thoron, arsenazo, and the Schiff Base, it is possible to separate thorium and T.R.E.

When the Schiff Base is used, thorium can be quantitatively separated from T.R.E. in one operation. Thoron ** gives satisfactory results.

It is, however, more expedient to use the Schiff Base since this can be readily prepared in the laboratory. Using thoron, it is possible to separate up to 148 γ of thorium (Table 2) in one adsorption.

*Prepared from salicaldehyde and o-aminoarsonic acid.

**Issued by Russian industry.

TABLE 2

Separation of Thorium from T.R.E. in the Form of Different Complex Compounds by Means of Activated Charcoal (in 30 ml solution with 218 γ Th and 215 γ of T.R.E.)

| Reagent | Optimum acidity for color development | Distribution, in γ | | | |
|---|---|---|---|---|---|
| | | charcoal | | solution | |
| | | $Th^{4+}$ | T.R.E. | $Th^{4+}$ | T.R.E. |
| Thoron | 0,05—0,1 *N* | 148 | — | 55 | 210 |
| Arsenazo | 0,05—0,1 *N* | 80 | — | 130 | 200 |
| Pyrocatechol violet | pH 2,4—3 | 220 | 122 | — | 110 |
| Hydroxyhydroquinone rose | pH 2,4—3 | 208 | 160 | — | 50 |
| Quinalizarin | pH 3—4 | 220 | 180 | — | 20 |
| Schiff Base | 0,05—0,1 *N* | 208 | — | — | 220 |

Zirconium behaves like thorium.

Separation of the rare earths from accompanying metals by the method of "in situ nascendi" reagents. The method of "in situ nascendi" reagents was also used for separating T.R.E. from accompanying metals. The oxalate ion which is formed during the hydrolysis of acetonedioxalic acid gives coarse-crystalline precipitates of the oxalates of the rare earths [2].

To 100 ml of a hydrochloric acid solution (pH about 5) containing T.R.E., thorium, iron, titanium, and zirconium in the amounts indicated in Table 3, was added 0.5 ml of a 25% solution of calcium chloride (25 mg calcium) and 15 ml of a solution of acetonedicarboxylic acid corresponding to about 4 g of oxalate ions. The solution was boiled on a closed asbestos electric hot plate for 15 minutes; on the second day after mixing, the precipitate was filtered through a double "white band" filter 9 cm in diameter, and washed 4-5 times with a 1% solution of oxalic acid. The precipitate was transferred to a porcelain crucible and calcined at 700°. The residue obtained was transferred to a 100 ml beaker, moistened with water, and 3-4 ml of hydrochloric acid sp. gr. 1.19 added. The acid was evaporated until a moist residue of salts was obtained; the chlorides of T.R.E., thorium, and calcium were dissolved in 30 ml of water and the acid neutralized with 10% ammonia solution using congo-red paper as indicator (pH about 4), 0.5 ml of hydrochloric acid sp. gr. 1.12 was then added, followed by 2 ml of a 0.1% solution of thoron, and, after mixing, 0.1 g of activated wood charcoal added. The solution was mixed for 20-25 seconds and filtered through a "white band" filter, 9 cm in diameter. This operation was repeated. After removal of thorium (and traces of zirconium) from the T.R.E., ammonia solution was added until the pH was 4 (blue-violet color of congo paper), and the solution transferred to a 50 ml standard flask; the volume was made up to the mark with water and T.R.E. determined. For this purpose equal aliquot parts of the solution obtained — from 2 to 10 ml — were transferred to two 25 ml standard flasks.

One of these solutions was used as a reference solution, while the other was used for colorimetric measurements. To the reference solution was added 0.5 ml of a 1% solution of ascorbic acid, 0.35 ml of 10% tartaric acid, 3 ml of a 0.05% arsenazo solution, and 4 ml of 20% urotropine solution; the volume was then made up to the mark with water and mixed. To the solution to be used for colorimetric measurements was added 0.5 ml of 1% ascorbic acid, 0.5 ml of 10% sulfosalicylic acid, 3 ml of 0.05% arsenazo solution, and 4 ml of 20% urotropine solution; the volume was made up to the mark with water, the whole was thoroughly mixed and colorimetric measurements made after 30 minutes.

A calibration curve was constructed as follows: into 14 standard flasks of 25 ml capacity were introduced various amounts of a standard solution of the T.R.E. containing 5-10-15....70 γ T.R.E., calcium chloride solution equivalent to 5 mg of calcium was added to each flask, followed by 0.5 ml of 10% sulfosalicylic acid, 3 ml of 0.05% arsenazo solution, and 4 ml of 20% urotropine solution. The solutions were mixed and the optical density measured after 30 minutes as indicated above. The reference solution was prepared in the same way, but with omission of the T.R.E.

Completely satisfactory results were obtained (Table 3).

TABLE 3

Separation of T.R.E. from Accompanying Elements

| Taken | | | | | T.R.E. found, in γ | Error in T.R.E., in γ |
|---|---|---|---|---|---|---|
| $Fe^{3+}$, mg | $Ti^{4+}$, mg | $Zr^{4+}$, mg | $Th^{4+}$ γ | T.R.E., in γ | | |
| 50,0 | 5,0 | 5,0 | 268,0 | 50,0 | 56,0 | + 6,0 |
| 50,0 | 5,0 | 5,0 | 175,7 | 84,0 | 97,5 | +13,5 |
| 50,0 | 5,0 | 5,0 | 200,0 | 127,2 | 125,0 | — 2,2 |
| 50,0 | 5,0 | 5,0 | 200,0 | 169,6 | 160,0 | — 9,6 |
| 50,0 | 5,0 | 5,0 | 200,0 | 254,4 | 245,0 | — 9,4 |
| 50,0 | 10,0 | 10,0 | 200,0 | 212,0 | 215,0 | + 3,0 |
| 50,0 | 10,0 | 10,0 | 200,0 | 212,0 | 215,0 | + 3,0 |
| 50,0 | 5,0 | 5,0 | 200,0 | 127.2 T.R.E. +118,0 $Y_2O_3$ 245,2 | 255,0 | + 9,8 |

Determination of total rare earths in materials with a complex composition. 1 g of dry sodium peroxide was placed in a 10 ml porcelain crucible; this was followed by 0.0250-0.2500 g of sample and a further 3-4 g of sodium peroxide. The crucible was placed inside a large crucible and transferred to a muffle furnace

TABLE 4

Photometric Determination of T.R.E. in Synthetic Mixtures

| Main components | Sample wt., in g | T.R.E. content, in % | T.R.E. found, in % | Error, in % |
|---|---|---|---|---|
| $SiO_2$ 50,0; $Fe_2O_3$ 3,0 | 0,1565 | 0,21 | 0,21 | |
| $Al_2O_3$ 12,0; CaO 12,0 | 0,1182 | | 0,22 | +9,5 |
| $ThO_2$ 0,1 | 0,0886 | | 0,26 | |
| Ditto + 5,0 $ZrO_2$ | 0,0800 | 0,21 | 0,22 | +4,8 |
| +10,0 $TiO_2$ | | | | |
| Ditto | 0,0820 | 2,0 | 1,95 | —2,5 |
| Ditto | 0,0310 | 2,0 | 1,97 | —1,5 |

heated to 300°. The temperature was taken up to 550° and fusion carried out until a homogenous melt was obtained. The cooled melt was dissolved in 100 ml of water on heating in the course of 20-25 minutes. After cooling, the crucible was taken out of the beaker and the solution filtered through a 9 cm "white band" filter; the hydroxides on the filter paper were washed 2-3 times with water and dissolved in 20-30 ml of 5% (by volume) hot hydrochloric acid, a saturated solution of sodium acetate was then added dropwise until the pH was 5 (congo-red paper), the volume of the solution was made up to 100 ml and the procedure outlined above subsequently followed.

The results (Table 4 and 5) proved to be completely satisfactory, although considerable deviations were obtained sometimes (+27.0 and +49%). This is a consequence of the fact that the gravimetric method is not accurate enough.

Normal contents of up to 40% yttrium in ores and rocks may be 5-6% higher than the actual amount when this method is employed, but this is quite permissible.

TABLE 5

Determination of T.R.E. in Ores and Rocks

| T.R.E. content, in % | | T.R.E. found photometrically, in % | | Error, in % |
|---|---|---|---|---|
| determined gravimetrically | T.R.E. added | with addition of T.R.E. | without addition of T.R.E. | |
| 2,27 | — | — | 2,20 | +3,0 |
| 0,97 | — | — | 1,07<br>0,90 | + 1,6 |
| 0,13 | 0,10 | 0,25 | 0,14 | + 7,0 |
| 0,11 | 0,10 | 0,25 | 0,14 | +27,0 |
| 0,23 | 0,10 | 0,35 | 0,25 | + 9,0 |
| 0,08 | 0,10 | 0,18 | 0,07 | —14,0 |
| 0,21 | — | — | 0,17<br>0,19 | —16,6 |
| 0,047 | — | — | 0,07 | +49,0 |
| 0,39 | — | — | 0,38<br>0,40<br>0,43 | + 3,3 |
| 0,06 | — | — | 0,06<br>0,07 | + 8,3 |

## SUMMARY

It has been established that solutions of the complexes of the rare earths of the cerium and yttrium groups with arsenazo conform to Beer's law. Interference from calcium and other elements during photometric determinations can be prevented by means of sulfosalicylic and tartaric acids.

A method is suggested for separating small amounts of thorium from total rare earths.

A photometric method has been developed for the determination of 0.01 to 3% of total rare earths in ores and rocks with an experimental error of 5-20%. It takes 8-10 hours to carry out 8-10 analyses.

## LITERATURE CITED

[1] F.V. Zaikovskii and L. I. Gerkhardt, J. Anal. Chem. 13, 274 (1958).*

[2] F. V. Zaikovskii and L. I. Gerkhardt, J. Anal. Chem. 13, 513 (1958).*

[3] V. I. Kuznetsov, J. Anal. Chem. 7, 226 (1952).*

[4] V. I. Kuznetsov, J. Gen. Chem. 14, 902 (1944).

[5] V. Suk and M. Malat, Chemist-Analyst 45, N 2, 30 (1956).

[6] F. V. Zaikovskii and L. I. Gerkhardt, Bulletin VIMSa 1**, 35 (1956).

[7] A. Z. Purushotton, anal. Chem. 145, 245 (1955).

Received October 12, 1957

*Original Russian pagination. See C.B. Translation.

**Not identified. Perhaps All-Union Scientific Research Institute of Raw Materials (VIMS) — Publisher's note.

# GRAVIMETRIC AND PHOTOMETRIC DETERMINATION OF THE THORIUM CONTENT OF URANINITES BY MEANS OF ANTHRANILIC ACID

Yu. V. Morachevskii and I. A. Tserkovnitskaya

The A. A. Zhdanov Leningrad State University

Organic reagents have found wide application in recent years for the separation of thorium during the analysis of natural materials. Phenylacetic, anthranilic, phenylpropionic [1], naphthylacetic [2], o-chlorophenoxyacetic [3], acetylsalicylic, and guaiacolacetic acids [4] permit separation of thorium from the rare earths, but not from uranium. Thorium can be separated from uranium by means of ferron [1], and naphthionic and sebacic acids, etc [5, 6]. Meta-nitrobenzoic acid [1], o-chlorobenzoic and 2,4-dichlorophenoxyacetic acids have been suggested for the separation of thorium from uranium and the rare earths in each other's presence.

Most of the reagents listed have only been used by the authors for the separation of appreciable amounts of thorium. For isolating small amounts of thorium (less than 1 mg) only phenylacetic, phenylpropionic, and naphthyl acids have been used.

Natural uraninites, in addition to their high uranium content, and the presence of lead and the rare earths in them, contain relatively small amounts of thorium. It was of interest therefore to select a method for determining thorium, which would allow one to separate thorium easily, and finally determine the amount of thorium present. For this purpose we chose anthranilic acid.

Isolation of thorium from solutions by means of anthranilic acid. Anthranilic acid has not been used for isolating small amounts of thorium. An idea of the possibility of precipitating large amounts of thorium by means of this reagent can be gained from the work of Murthy and Rao [7].

We precipitated thorium as follows. To a thorium nitrate solution heated to the boiling point was added 0.5 g of ammonium acetate and various amounts of a 0.35% aqueous solution of anthranilic acid; after boiling for two minutes, the precipitate was filtered off, washed a few times with hot water and then calcined to $ThO_2$. The volume did not exceed 50 ml in any of the experiments.

It follows from the results given in Table 1, that under certain conditions, thorium can be quantitatively precipitated by means of anthranilic acid; a large excess of precipitant does not interfere with complete separation.

In order to establish the optimum acidity for carrying out the precipitation, thorium was precipitated with anthranilic acid at various pH values of the solution; the pH was regulated by an acetate buffer mixture.

Quantitative deposition of thorium anthranilate was found to occur in the pH range 4.2 to 5.6 (Table 2). Further increases in the pH of the solution led to partial dissolution of thorium anthranilate.

Precipitation of thorium in the presence of uranium. It was established that it is best to precipitate thorium in the presence of uranium at a pH of 4.2-4.4; nevertheless, under these conditions, up to 30% of the uranium is coprecipitated with the thorium. In order to keep uranium in solution we complexed it with hydroxylamine hydrochloride. The addition of hydroxylamine to the solution does not prevent precipitation of thorium by anthranilic acid.

In order to establish what are the maximum amounts of uranium in whose presence thorium can still be precipitated with anthranilic acid, various amounts of uranyl nitrate were added to solutions containing 3 mg $ThO_2$ so that the ratio of $ThO_2$: $U_3O_8$ in the final solutions amounted to 1 : 10, 1 : 15, 1 : 50, and 1 : 100. 1 g

TABLE 1

(6.0 mg $ThO_2$ taken)

| Amount of anthranilic acid, in mg | $ThO_2$ found, in mg | Error, in mg |
|---|---|---|
| 3.5 | 5.2 | −0.8 |
| 7.0 | 5.2 | −0.8 |
| 14.0 | 5.8 | −0.2 |
| 20.0 | 6.0 | 0 |
| 35.0 | 6.1 | +0.1 |
| 52.0 | 6.0 | 0 |
| 70.0 | 6.1 | +0.1 |

TABLE 2

(6.0 mg $ThO_2$ taken)

| pH | $ThO_2$ found, in mg | Error, in mg | pH | $ThO_2$ found, in mg | Error, in mg |
|---|---|---|---|---|---|
| 3.7 | 0 | −0.6 | 5.0 | 5.9 | −0.1 |
| 4.0 | 5.6 | −0.4 | 5.2 | 6.1 | +0.1 |
| 4.3 | 5.9 | −0.1 | 5.4 | 5.9 | −0.1 |
| 4.5 | 6.0 | 0 | 5.6 | 5.9 | −0.1 |
| 4.6 | 6.1 | +0.1 | 6.0 | 4.8 | −1.2 |
| 4.8 | 6.0 | 0 | 6.2 | 4.6 | −1.4 |

of hydroxylamine hydrochloride and 0.5 g of ammonium acetate was added to each solution, and a dilute ammonia solution free from $CO_2$ used for adjusting the pH of the solution to the required value, methyl orange being used as indicator. The solution was then heated and thorium precipitated with 10 ml of a 0.35% solution of anthranilic acid. After being allowed to stand for 15 minutes, the precipitate was filtered, washed with hot water, and then calcined to $ThO_2$. In order to ensure more complete removal from uranium, the precipitate was reprecipitated. For this purpose the precipitate of thorium anthranilate was dissolved in dilute 1 : 5 nitric acid, the latter being added dropwise, 1 g of hydroxylamine hydrochloride was added and the pH controlled as during the first precipitation; thorium was then precipitated again with 0.35% reagent solution.

TABLE 3

(3.0 mg $ThO_2$ taken)

| $U_3O_8$ taken, in mg | $ThO_2$ found, in mg | Error, in mg |
|---|---|---|
| 30.0 | 3.10 | +0.1 |
| 50.0 | 3.15 | +0.15 |
| 150.0 | 3.20 | +0.2 |
| 300.0 | 3.30 | +0.3 |

TABLE 4

(8.0 mg $ThO_2$ taken)

| $CeO_2$ taken, in mg | $ThO_2$ found, in mg | Error, in mg |
|---|---|---|
| 6.0 | 8.0 | 0 |
| 12.0 | 8.0 | 0 |
| 18.0 | 8.0 | 0 |
| 24.0 | 8.1 | +0.1 |
| 36.0 | 8.1 | +0.1 |
| 66.0 | 8.2 | +0.2 |
| 128.0 | 8.7 | +0.7 |

It follows from the results given in Table 3, that by complexing sexivalent uranium with hydroxylamine, it is possible to separate fairly small amounts of thorium from uranium in amounts which are considerably in excess of that of the thorium.

Similar experiments were carried out on the separation of thorium by means of anthranilic acid in the presence of the rare earths and lead (Tables 4 and 5).

According to these results, up to ratios of $ThO_2$: $CeO_2$ = 1 : 8, thorium is almost completely separated from the rare earths by means of anthranilic acid. Lead, as the results given in Table 5 show, is not precipitated by means of anthranilic acid under the experiments conditions used.

Photometric determination of thorium. According to Murthy and Rao's results [7] the salt formed between thorium and anthranilic acid has a definite composition which corresponds to the formula $[(C_7H_6O_2N)_2(ThOH)_2]$. On the other hand, it is known that during diazotization of anthranilic acid and subsequent treatment with β-naphthol there is formed an orange dye [8]. The dye formed is azo-β-naphtho-β-benzoic acid. We thought it would be of interest therefore to use the colored compound obtained by diazotization for the photometric determination of the thorium anthranilate isolated. This would permit the limits of applicability of this method to be extended considerably.

TABLE 5

(5.0 mg $ThO_2$ taken)

| PbO taken, in mg | $ThO_2$ found, in mg | Error, in mg |
|---|---|---|
| 10.0 | 5.1 | +0.1 |
| 20.0 | 5.2 | +0.2 |
| 40.0 | 5.1 | +0.1 |
| 50.0 | 5.2 | +0.2 |
| 60.0 | 5.2 | +0.2 |
| 75.0 | 5.3 | +0.3 |

Calibration curve for the determination of thorium.

Conditions for obtaining the colored compound were chosen first. Diazotization was carried out in hydrochloric acid solution with cooling. For this operation we used a 4% solution of sodium nitrate and a 1% solution of β-naphthol in 5% sodium hydroxide. The optimum amounts of the reagents participating in the reaction are: 1 ml of NaOH and 1 ml of β-naphthol in 50 ml of solution. At a pH of 1.6-2.6 for the original solution, a bright-orange precipitate of the azo dye separated out; the dye was insoluble in alkali. At a pH of 2.9-4.0 transparent brightly colored solutions of the dye were obtained. At a pH of 5 and higher the solutions did not become colored on addition of β-naphthol.

The color shade of the dye can change from yellow orange to lemon yellow depending on the pH of the solution.

The most suitable shade for photometric measurements proved to be the yellow-orange shade obtained at a pH of 2.9-4.0. The absorption maxima for the dye lie at 280 and 340 mμ. The optical density of the colored solution remains constant over several days. When pure anthranilic acid was used, it was found that there was a linear relation between the color of the dye formed by diazotization and the concentration of anthranilic acid.

TABLE 6

| $ThO_2$ taken, in mg | $ThO_2$ found, in mg | Error, in mg |
|---|---|---|
| 0.50 | 0.525 | 5.0 |
| 0.50 | 0.520 | 4.0 |
| 0.36 | 0.360 | 0 |
| 0.30 | 0.310 | 3.3 |
| 0.30 | 0.290 | 3.3 |
| 0.20 | 0.190 | 5.0 |

For determination of thorium in solution containing from 0.2 to 0.5 g of $ThO_2$ in the form of the nitrate, precipitation with anthranilic acid was carried out as indicated above. The precipitated thorium anthranilate was carefully washed with hot water and alcohol for removing excess free anthranilic acid. The precipitate was then dissolved in 25 ml of 0.1 N HCl and the solution transferred to a 50 ml standard flask, and the volume made up to the mark with distilled water. Aliquots which were taken from this solution (10-20 ml, depending on the intensity of the color of the dye formed) were cooled, and 1 ml of 4% $NaNO_2$ and 1 ml of 1% β-naphthol solution added. The solutions were diluted to a volume of 50 ml in standard flasks and the color measured in 10 ml cells, using a blue filter; distilled water was used as the reference solution. The $ThO_2$ content was established by means of a calibration curve.

As the results given in Table 6 shows, the experimental error of the method amounts to 3-5%.

Determination of thorium in uraninite by means of anthranilic acid. We adopted the following method for isolating and determining thorium during the analysis of uraninites: 25-400 mg of the uraninite was dissolved

in 10 ml of $HNO_3$ (1 : 5). The solution was heated until nitrogen oxide fumes were liberated, 20 ml of water was added, followed by 1-2 g of hydroxylamine hydrochloride; the pH of the solution was then adjusted by addition of 0.5 g of ammonium acetate and dilute 1% ammonia solution, using methyl orange as indicator.

The solution was heated to the boiling point and thorium precipitated with 20 ml of a 0.35% aqueous solution of anthranilic acid. After standing for 15 minutes, the precipitated thorium anthranilate was filtered off, washed with hot water, and then reprecipitated. The latter was carried out by washing the precipitate off the filter with 25 ml of dilute HCl (1 : 10) into a beaker; 1 g of hydroxylamine hydrochloride was added again, the pH was adjusted to about 4.5, and the thorium precipitated again with anthranilic acid as indicated above.

The thorium anthranilate precipitate was calcined and then weighed as $ThO_2$, or the thorium was determined photometrically as indicated above.

The results obtained are compared below in Table 7 with those obtained by precipitation of thorium with phenylacetic acid, which was carried out during the systematic analysis of uraninite.

TABLE 7

| Uraninite sample no. | Sample weight, in mg | $ThO_2$, as found by the anthranilic acid method | | | $ThO_2$, as found by the phenylacetic acid method |
|---|---|---|---|---|---|
| | | in mg | in % | mean value | |
| 1* | 356,7 | 9,5 | 2,63 | 2,58 | 2,60 |
| | 138,2 | 3,7 | 2,69 | | |
| | 138,0 | 3,5 | 2,46 | | |
| | 123,9 | 2,2 | 2,58 | | |
| 2* | 295,0 | 7,1 | 2,40 | 2,36 | 2,30 |
| | 335,0 | 7,9 | 2,36 | | |
| | 287,8 | 6,8 | 2,37 | | |
| | 443,9 | 10,3 | 2,34 | | |
| 3** | 26,8 | 0,44 | 1,64 | 1,65 | 1,60 |
| | 46,8 | 0,76 | 1,60 | | |
| | 46,6 | 0,80 | 1,73 | | |
| 3** | 37,5 | 0,83 | 2,21 | 2,23 | 2,24 |
| | 24,8 | 0,66 | 2,26 | | |

*Gravimetric determination.

**Photometric determination.

The method suggested for the isolation of thorium in the form of its anthranilate, and its subsequent photometric determination after diazotization of the anthranilate, gives results which are in good agreement with the longer analytical methods.

## SUMMARY

1. A study has been made of the possibility of separating thorium in the presence of uranium, the rare earths and lead, by means of anthranilic acid. It has been shown that thorium can be quantitatively precipitated at concentrations not less than 0.2 mg/50 ml.

2. A photometric method for determining thorium is suggested, which is based on formation of a colored compound as a result of the reaction between anthranilic acid, nitrous acid, and β-naphthol. The method is highly sensitive, and permits determination of down to 0.04 γ of Th/ml. The method of isolating and determining thorium has been applied to the analysis of natural uraninites, and has given completely satisfactory results.

## LITERATURE CITED

[1] K. Rodden, "Analytical Chemistry of Uranium and Thorium," IL, Moscow (1956).*

[2] S. K. Datta and G. Banerjee, Analyt. chim. acta 12, 38 (1955).

[3] L. Gordon, C. C. Yauselow, and H. H. Willard, Analyt. Chem. 21, (1949).

[4] Rao Lakshmana and Rao. Bh. Raghava, J. Indian. Chem. Soc. 27, 569, 610 (1950).

[5] Rao M. Nageswara and Rao Rh S. V. Raghava, Z. analyt. Chem. 142, 27 (1954).

[6] S. K. Data and J. J. Bauerjee, J. Indian. Chem. Soc, 31, 929 (1954).

[7] Rao M. and Murthy, Indian Chem. Soc. 18, 459 (1951).

[8] K. Bauer, "Analysis of Organic Compounds", IL, Moscow, 1953, pp. 92, 279.*

Received September 1, 1957

*Russian translation.

# KINETIC METHODS OF QUANTITATIVE ANALYSIS. COMMUNICATION 5. A KINETIC METHOD FOR THE DETERMINATION OF TANTALUM

K. B. Yatsimirskii, O. M. Drobysheva, and V. I. Rigin

Ivanov Chemico-Technological Institute

In previous articles [1, 2] we have dealt with kinetic methods of determining molybdenum and tungsten, which were based on the catalysis of the oxidation of iodide by hydrogen peroxide in an acid medium. In the work described here the catalysis of this reaction by Ta(V) compounds was used for developing a kinetic method for the quantitative determination of low concentrations of tantalum.

The working solutions were 0.01 M solutions of KI and $H_2O_2$, a 1 M solution of HCl, and a 0.2% starch solution. All the reagents were given special purification to free them from heavy metals.

The tantalum solution was prepared by fusing an aliquot of $Ta_2O_5$ with potassium pyrosulfate and leaching the melt with a saturated solution of ammonium oxalate. The tantalum content of the solution was established by means of the tannin method.

The theoretical principles of kinetic methods of chemical quantitative analysis have been discussed in detail previously [3].

The following technique was used. Into a 50 ml standard flask was introduced the solution of tantalum, followed by potassium iodide and starch, and the volume made up to a volume of 40-43 ml and then thoroughly mixed. To this solution was then added the requisite amount of hydrogen peroxide, and the volume made up to the mark with water, the whole was mixed again and finally introduced into the cell of a FEK-M photocolorimeter. At the moment the hydrogen peroxide was added to the solution a stop watch was started, and the optical density then measured at equal time intervals. The initial concentrations of the reactant were as follows: tantalum, from $2 \times 10^{-6}$ to $5 \times 10^{-5}$ M; potassium iodide, from $2 \times 10^{-4}$ to $2 \times 10^{-3}$ M; hydrogen peroxide, from $2 \times 10^{-4}$ to $2 \times 10^{-3}$; and hydrochloric acid, from 0.1 to 0.5 M.

The optical density of the solution is proportional to the concentration of the liberated iodide, while the change of optical density in unit time is proportional to the rate of reaction. The over-all equation of the reaction is:

$$H_2O_2 + 2I^- + 2H^+ \rightleftarrows I_2 + 2H_2O. \qquad (1)$$

In order to establish the form of the equation of the reaction rate, a study was made of the relation between the reaction rate and the concentration of the individual reagents. The results obtained are shown graphically in Figs. 1-4. On the basis of an analysis of the results obtained, the equation for the rate of reaction can be written as follows:

$$d[I_2]/d\tau = (\varkappa_0 + \varkappa_1 C_{H^+}) \cdot C_{I^-} \; C_{H_2O_2} \cdot C_{Ta}, \qquad (2)$$

where $C_I$, $C_{H_2O_2}$, $C_{H^+}$, and $C_{Ta}$ are the concentrations of iodide, hydrogen peroxide, acid, and catalyst (Ta), respectively, $\kappa$ is the catalytic coefficient (reaction rate constant). The curve relating the reaction rate and hydrogen ion concentration does not pass through the origin; this can be explained on the grounds that the reaction proceeds in two direction [4].

The curve relating reaction rate and tantalum concentration (the concentrations of the other reagents being constant) is, in essence, a calibration curve for the determination of Ta.

The effect of foreign ions on the accuracy of tantalum determination by the given method was studied.

Effect of Foreign Ions

| Ion | Conc. of foreign ion, in mole/liter | Ratio of conc. | Tangent $\alpha$, $min^{-1} \cdot 10^2$ | Relative error | Ion | Conc. of foreign ion in mole/liter | Ratio of conc. | Tangent $\alpha$, $min^{-1} \cdot 10^2$ | Relative error |
|---|---|---|---|---|---|---|---|---|---|
| $K^+$ | $10^{-2}$ | 1:1000 | 0,33 | —3 | $F^-$ | $10^{-3}$ | 1:10 | 0,04 | —88 |
| $Na^+$ | $10^{-2}$ | 1:1000 | 0,36 | +6 | $Cl^-$ | $10^{-4}$ | 1:10000 | 0,34 | 0 |
| $Mg^{2+}$ | $10^{-3}$ | 1:100 | 0,37 | +9 | $NO_3^-$ | $10^{-1}$ | 1:100 | 0,39 | +14 |
| $Ca^{2+}$ | $10^{-3}$ | 1:100 | 0,32 | —6 | $ClO_4^-$ | $10^{-3}$ | 1:100 | 0,35 | +3 |
| $Al^{3+}$ | $10^{-3}$ | 1:100 | 0,32 | —6 | | | | | |
| $Zn^{2+}$ | $10^{-3}$ | 1:100 | 0,33 | —3 | | — | — | 0,34 | Reference solution |

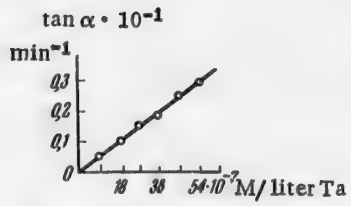



Fig. 1. Relation between reaction rate (1) and tantalum concentration. Concentrations of the solutions: KI — $1.0 \cdot 10^{-4}$ M; $H_2O$ — $1.0 \cdot 10^{-3}$ M; $H^+$ — 0.16 M.

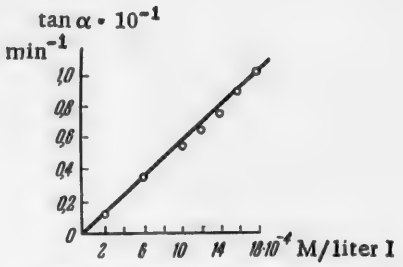



Fig. 2. Relation between reaction rate (1) and iodide concentration.

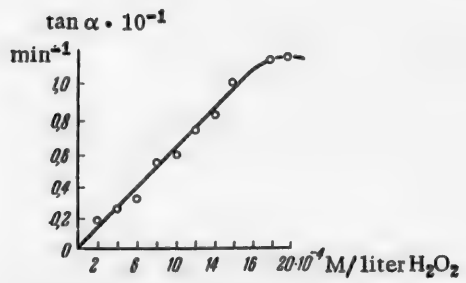



Fig. 3. Relation between reaction rate (1) and hydrogen peroxide concentration.

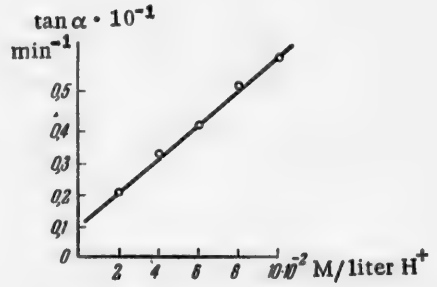



Fig. 4. Relation between reaction rate (1) and hydrogen ion concentration.

From this table it is clear that large amounts of cations and anions normally met, do not interfere with the determination of tantalum in solutions free from the ions of elements which catalyze the given reaction. Fluoride slows down the reaction by combining with tantalum to form a stable complex. The accelerating effect of nitrate is explained by traces of nitrite, which catalyzes the reaction.

Titanium and zirconium do not interfere with the reaction under the conditions indicated, since the oxalate complexes of these elements do not catalyze reaction (1). For the same reason, niobium, in equivalent amounts, or in amounts which are two-three times in excess, does not interfere with the determination of tantalum.

The rate of reaction (1) does not change essentially in the presence of sulfate ions, right up to a concentration of the latter of 0.1 M, accordingly, sulfate ions do not interfere with tantalum determination.

## SUMMARY

A new and highly sensitive method has been developed for the quantitative determination of tantalum. The effect of certain ions on the accuracy of the method has been studied.

## LITERATURE CITED

[1] K. B. Yatsimirskii and L. P. Afanas'eva, J. Anal. Chem. 11, 319 (1956).*

[2] K. B. Yatsimirskii and V. L. Rigin, J. Anal. Chem. 13, 112 (1958).*

[3] K. B. Yatsimirskii, J. Anal. Chem. 10, 339 (1955).*

[4] J. Brode, Z. phys. Chem. 37, 217 (1901).

Received January 20, 1958

*Original Russian pagination. See C.B. Translation.

# THE POLAROGRAPHIC PROPERTIES OF NIOBIUM IN PHOSPHORIC ACID SOLUTIONS

D. I. Kurbatov

Ural Branch of the USSR Academy of Sciences, Sverdlovsk

The polarographic properties of niobium have been studied mainly in weak nitric acid solutions and in solutions of certain complexing agents. Thus, Zeltzer [1], and Portnov [2] obtained a wave for niobium in weak nitric acid solution. Stromberg and Reinus [3, 4] carried out a detailed study of nitric acid solutions of niobium, and found that the wave height is proportional to its concentrations in the range 0.2-4 millimoles/ /liter. Dhar [5] reduced niobium in nitric acid solutions in the presence of $Cl^-$, $ClO_4^-$, and $SO_4^{2-}$. Elson [6], Ferrett and Milner [7, 8] studied the behavior of niobium in solutions of oxalic, tartaric, citric, ethylenediaminetetraacetic acids and in other acids.

In recent years several papers have been published on the polarography of $Nb^V$ in concentrated mineral acids. Cozzi and Vivarelli [9] found that niobium is reduced on the mercury cathode in hydrochloric acid solution.

Krylov, Kolevatova, and Samarina [10, 11] studied the polarographic properties of niobium in 70% sulfuric acid, and showed that niobium gives a well-defined wave on the dropping-mercury cathode, the height of the wave being proportional to the niobium concentration; cathodic reduction of $Nb^V$ is irreversible under these conditions.

Gokhshtein [12] while studying the reduction of niobium in 70% sulfuric acid, showed that $Nb^V$ gives a wave which is distorted by the discharge of hydrogen ions. In this connection, therefore, he recommends the use of an oscillographic polarograph, in which hydrogen ions do not have any effect, and the maxiumum current is proportional to niobium concentration.

The brief review shows that the polarographic properties of quinquevalent niobium on a dropping-mercury cathode in mineral acids have not been studied very much.

With the aim of extending the study of the polarographic properties of $Nb^V$ in mineral acid solutions, we investigated solutions of niobium in orthophosphoric acid.*

Concentrated phosphoric acid (1.75) was used for this work since the author [13] had previously shown that niobium phosphates are soluble in solutions of concentrated mineral acids.

The niobium solutions were prepared from spectrographically pure niobium pentoxide, by fusing an aliquot of the latter with potassium bisulfate. After cooling, the melt was dissolved in 1% sulfuric acid. Niobium hydroxide was precipitated from this solution by means of ammonia, the precipitate was boiled, it was then cooled and filtered through a glass filter. The precipitate was washed with dilute ammonia until it was free from $SO_4^{2-}$ ions. The niobic acid formed was dissolved in concentrated phosphoric acid and transferred to a standard flask in which the volume was made up to the mark with phosphoric acid and the whole thoroughly mixed. Polarographic measurements were carried out on a SGM-8 type polarograph made by the Geologorazvedka factory.

*G. M. Veikes, a student at the Lenin Kazan State University, participated in the experimental work.

The galvanometer scale was calibrated by measuring the current passing through a KMS-6 resistance box connected into the circuit instead of the electrolytic cell; the voltage applied was 1000 volt. At a sensitivity of 1/10, 1 mm on the scale was found to correspond to 0.03 μA.

The electrolytic cell used was either an H-shaped vessel, into one arm of which was poured mercury to serve as the anode, or a 90 mm tall beaker, the bottom of which was covered with mercury. The surface area of the anode was greater than 5 $cm^2$ in both cases.

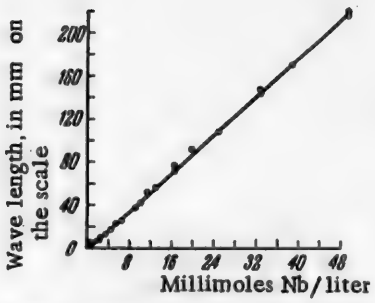



Fig. 1. Relation between the limiting current of niobium and the niobium concentration of the solution. Nb concentration expressed in millimoles/liter.

Curves were taken using a saturated calomel electrode (S = 5 $cm^2$) as the external anode. The bridge consisted of a Π-shaped tube filled with concentrated phosphoric acid; the ends of the tube were closed with plugs of glass wool.

In order to eliminate the diffusion potential, connection was established through a vessel containing a saturated solution of potassium chloride.

Hydrogen was passed through the solutions for 15-20 minutes before taking the current-voltage curves. The hydrogen used was prepared by internal electrolysis [14].

The temperature of the solutions being polarographed was kept constant at 25° by means of an universal thermostat.

The relation between the limiting current and the half-wave potential, and the niobium concentration, are given in the Table and in Fig. 1. It is clear from the Table and from Fig. 1 that the limiting current (wave height) increases linearly with increasing niobium concentration of the solution.

Relation between the Values of the Limiting Current and the Half-Wave Potential of Niobium in Phosphoric Acid Solutions, and the Niobium Concentration

($P = m^{2/3} \tau^{1/6} = 0.756\ mg^{2/3} \cdot sec.^{-1/2}$, at E = 1 volt)

| Concentration of niobium in solution | | Limiting current, in mm of the galvanometer scale (S = 1/5) | $\frac{I_d}{C_{Nb}}$, in mM/liter | $E_{1/2}$ (saturated calomel electrode) |
|---|---|---|---|---|
| g/liter | mM/liter | | | |
| 0,046 | 0,5 | 4,4 | 8,8 | 0,610 |
| 0,0910 | 0,98 | 8,4 | 8,6 | 0,605 |
| 0,1132 | 1,2 | 8,8 | 7,4 | 0,605 |
| 0,221 | 2,38 | 17,2 | 7,3 | 0,600 |
| 0,354 | 3,54 | 25,8 | 7,3 | 0,615 |
| 0,4224 | 4,55 | 33,0 | 7,3 | 0,607 |
| 0,517 | 5,54 | 42,6 | 7,7 | 0,610 |
| 0,606 | 6,5 | 49,8 | 7,65 | 0,615 |
| 0,692 | 7,45 | 55,5 | 7,46 | 0,610 |
| 0,775 | 8,35 | 64,0 | 7,65 | 0,610 |
| 0,854 | 9,15 | 75 | 8,2 | 0,620 |
| 0,929 | 9,96 | 82 | 8,2 | 0,610 |
| 1,072 | 11,6 | 102 | 8,8 | 0,610 |
| 1,204 | 12,9 | 112 | 8,6 | 0,610 |
| 1,548 | 16,65 | 141 | 8,3 | 0,625 |
| 1,858 | 20 | 180 | 9,0 | 0,640 |
| 2,322 | 25 | 216 | 8,65 | 0,650 |
| 3,090 | 33,2 | 288 | 8,65 | 0,657 |
| 3,71 | 39,0 | 372 | 8,75 | 0,665 |
| 4,645 | 50 | 438 | 8,75 | 0,680 |
| | | Mean | 8,1 | 0,622 |

The linear relation between the limiting current of niobium and its concentration in solution, together with the clearly defined wave (Fig. 2) permit niobium to be determined quantitatively in solution by a polarographic method.

The solutions are stable over a prolonged period (months) and give readily reproducible polarograms.

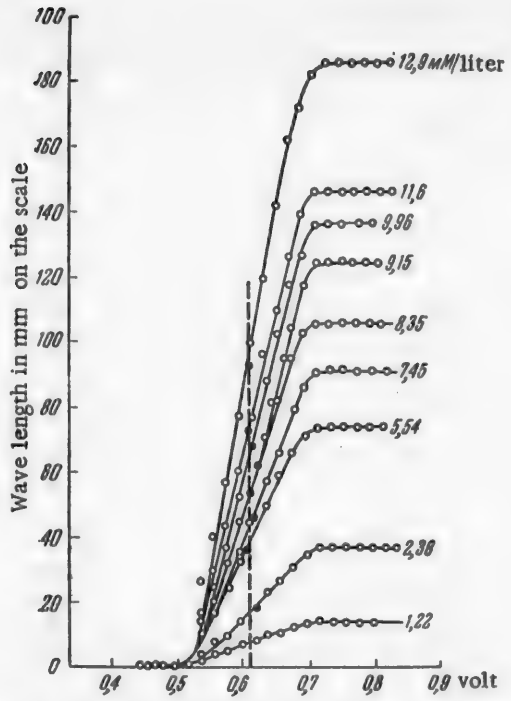



Fig. 2. Niobium waves in concentrated phosphoric acid for different niobium concentrations. Niobium concentration expersed in mM / liter.

The general appearance of the i - E curves (Fig. 2) show that reduction of niobium proceeds in one stage. It is also clear from the Table that the half-wave potential ($E_{1/2}$) increases from 0.600 to 0.680 volt with respect to the saturated calomel electrode, with increasing niobium concentration.

In order to establish whether or not the electrode process is reversible, we calculated and constructed the curve relating log $i/(i_d - i)$ and the change in applied potential E (Fig. 3).

An examination of the results obtained (Fig. 3) shows that reduction of $Nb^V$ from phosphoric acid solutions is irreversible. The slope has a value of 0.080,

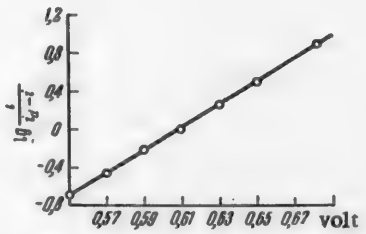



Fig. 3. Relation between the potential E and log $i/(i_d - i)$ for niobium (V) waves.

which differs essentially from the value calculated by means of the equation for a polarographic wave.

A study of the effect of diluting the phosphoric acid (1.75) with water showed that addition of 15% of water has no effect on the half-wave potential of niobium. Further addition of water leads to distortion of the niobium wave by the hydrogen wave. Addition of gelatine in amounts ranging from 0.01 to 0.1% showed no effect on the wave height.

Thus, phosphoric acid is preferable to nitric and sulfuric acids as a supporting electrolyte for the polarographic determination of niobium. Solutions of niobium in phosphoric acid are stable, and give a clearly defined wave for niobium within the concentration range 0.2-50 millimoles / liter. When nitric acid is used, the linear relation between the limiting current and niobium concentration only holds for the concentration range 0.2 to 4 millimoles/ liter, while in sulfuric acid solutions the niobium wave is distorted by the discharge of hydrogen ions. Studies of the polarographic properties of niobium and of the elements which accompany it, in acid solutions, continue.

## SUMMARY

A polargraphic study of phosphoric acid solutions of niobium has been carried out for the first time. It has been established that in concentrated phosphoric acid (1.75), niobium gives a clearly defined wave. The value of the limiting current is linearly related to the niobium concentration over the concentration range 0.5 to 50 millimole/ liter. Solutions of niobium in phosphoric acid are stable and give readily reproducible polarograms.

The half-wave potential $E_{1/2}$ increases from 0.600 to 0.680 volt (with respect to the saturated calomel electrode) as the niobium concentration increases (from 0.5 to 50 millimole/liter).

Reduction of $Nb^V$ in phosphoric acid solutions is irreversible.

## LITERATURE CITED


[1] S. Zeltzer, Collection Chechoslov. Chem. Commun., 4, 319 (1932).

[2] M. A. Portnov, Collection of Articles given at the 120'th anniversary of GIPKh, GNTI, Leningrad, 1939, p. 100.

[3] A. G. Stromberg and L. M. Reinus, J. Phys. Chem. 20, 693 (1946).

[4] A. G. Stromberg and L. M. Reinus, Trans. Commission on Anal. Chem. Vol. 2 (V), 1949, p. 34.

[5] S. K. Dhar, Analyt. chim. acta 11, 289 (1954).

[6] R. Elson, J. Amer. Chem. Soc., 75, 17, 4193 (1953).

[7] D. Ferrett and J. W. C. Milner, J. Chem. Soc. 5, 1186 (1956).

[8] D. Ferrett and J. W. C. Milner, Nature 175, 477 (1955).

[9] D. Cozzi and S. Vivarelli, Ricerca scient. 23, 12 224 (1953); Z. Electrochem. 58, 177 (1954).

[10] E. L. Krylov, V. S. Kolevatova, and V. A. Samarina, Proc. Acad. Sci. 98, 593 (1954).

[11] E. L. Krylov and V.S. Kolevatova, J. Anal. Chem. 11, 144 (1956).*

[12] Ya. P. Gokhshtein, Industrial Labs. 22, 1, 38 (1956).

[13] D. I. Kurbatov and N. V. Demenev, J. Appl. Chem. 29, 1747 (1956).*

[14] J. Heyrovsky, "Polarographic Method, Theory, and Practical Application," ONTI, Leningrad, 1937.**



Received November 10, 1957


*Original Russian pagination. See C.B. Translation.

**Russian translation.

# DETERMINATION OF NIOBIUM IN THE PRESENCE OF TUNGSTEN BY MEANS OF CUPFERRON

A. I. Ponomarev and A. Ya. Sheskov'skaya

The A. A. Baikov Institute of Metallurgy, Acad. Sci. USSR, Moscow

One of the complicated problems of analytical chemistry is the separation of niobium and tungsten. The difficult of carrying out a determination of niobium in the presence of tungsten is explained by the similarity of the properties of these elements. Tungsten, like niobium, gives oxides which are insoluble in water, and while carrying out the hydrolytic separation of niobium, tungsten also separates out [1]. Schoeller, Powell, and Jahn [2] separated niobium and tungsten by means of a mixture of magnesium sulfate, ammonium chloride, and ammonia in a carbonate solution after fusing tungsten and niobium oxides with potassium carbonate. Determination of niobium is completed by precipitation with tannin. Golubtsova [3] modified Schoeller's method somewhat, by replacing potassium carbonate by a mixture of sodium and potassium carbonates; the fusion rate is thereby increased. In addition, she established that increasing the amount of ammonia added to 5 ml, instead of the drops suggested by Schoeller, favors a more complete separation of niobium and tungsten. Budanova and Gavrilova [4], during determination of niobium and tungsten in steel, precipitated niobium together with iron, tantalum, and vanadium by means of cupferron in a sulfuric acid medium, using sodium fluoride as a complexing agent for tungsten. Under these conditions niobium is not precipitated completely quantitatively. Determination of niobium is completed by the acid hydrolysis method.

Our problem was to develop a method for determining niobium in alloys, steels, and other products containing tungsten, without having to resort to a preliminary separation of niobium and tungsten.

In order to study the conditions for precipitating and separating niobium from tungsten by means of cupferron, we prepared three standard solutions of niobium with oxalic acid, ammonium oxalate, and tartaric acid, respectively. The standard tungsten solution was prepared from sodium tungsten.

To accurately measured volumes of the standard niobium solution containing from 0.8 to 4.5 mg Nb, was added various amounts of the standard tungsten solution containing from 30 to 125 mg of W. The ratios of Nb : W were 1 : 25 and 1 : 35. The solutions were diluted with water to 100-150 ml, acidified with 5 drops of hydrochloric acid (sp. gr. 1.19) and the niobium precipitated with 10-20 ml of a 3% aqueous solution of cupferron; the latter was added slowly, dropwise, the solution being stirred continuously. A small amount of macerated paper was then added and the solution stirred until the precipitate had been completely coagulated. The precipitate was filtered through a 7-9 cm diameter paper (white band) and washed 5-6 times with cold water containing 20 ml of 3% aqueous solution of cupferron and 1 ml of hydrochloric acid (sp. gr. 1.19) per liter; the precipitate was then ashed in a platinum crucible or basin, and heated in a muffle until all the carbon of the filter paper had been burnt off; the residue was fused with 1-2 g of potassium pyrosulfate over a small burner flame to avoid sputtering. On cooling, 10-20 ml of a 4% oxalic acid or ammonium oxalate solution, or 10% tartaric acid was added to the contents of the crucible or basin and the contents of the crucible or basin heated on a sand bath until the melt had dissolved. This solution was transferred to a 250-300 ml beaker and the volume adjusted to 100-150 ml, this liquid was acidified with 5 drops of hydrochloric acid and the niobium precipitated as described above. Filter and precipitate were placed in a tared platinum or porcelain crucible in which they were ashed, the ash was then heated for 5-10 minutes at 1000° and niobium weighed as the pentoxide.

Niobium was precipitated with cupferron at room temperature. The precipitate was filtered rapidly, washed thoroughly, and was readily transferred onto the filter.

Results for the determination of niobium in a standard solution, in the presence of tungsten, are given in Table 1.

TABLE 1

Determination of Niobium in the Presence of Tungsten in a Standard Solution

| Complexing agent | Amount taken, in mg | | Nb, found, in mg | Difference, in mg |
|---|---|---|---|---|
| | W | Nb | | |
| Tartaric acid | 30 | 0,84 | 0,84 | 0,00 |
| | 30 | 0,84 | 0,98 | +0,14 |
| | 60 | 0,84 | 0,91 | +0,07 |
| | 50 | 1,68 | 1,75 | +0,07 |
| | 50 | 1,68 | 1,68 | 0,00 |
| | 50 | 1,68 | 1,75 | +0,07 |
| | 100 | 4,48 | 4,55 | +0,07 |
| | 100 | 4,48 | 4,55 | +0,07 |
| Ammonium oxalate | 30 | 2,17 | 2,24 | +0,07 |
| | 30 | 2,17 | 2,17 | 0,00 |
| | 30 | 2,17 | 2,10 | —0,07 |
| | 60 | 2,17 | 2,24 | +0,07 |
| | 60 | 2,17 | 2,24 | +0,07 |
| | 60 | 2,17 | 2,31 | +0,14 |
| | 50 | 4,48 | 4,27 | —0,21 |
| | 50 | 4,48 | 4,55 | +0,07 |
| | 50 | 4,48 | 5,55 | +0,07 |
| | 100 | 4,48 | 4,55 | +0,07 |
| | 100 | 4,48 | 4,55 | +0,07 |
| Oxalic acid | 100 | 4,48 | 4,62 | +0,14 |
| | 100 | 4,48 | 4,55 | +0,07 |
| | 100 | 4,48 | 4,48 | 0,00 |
| | 125 | 4,48 | 4,48 | 0,00 |
| | 125 | 4,48 | 4,27 | —0,21 |

TABLE 2

Reproducibility of the Results for the Determination of Nb in Alloys Containing from 36 to 70% of W

| Sample | Nb, in % | | |
|---|---|---|---|
| 32 | 50,64 | 50,70 | 50,76 |
| 33 | 42,50 | 42,51 | 42,75 |
| 34 | 34,16 | 34,17 | 34,73 |
| 35 | 21,38 | 21,47 | 21,50 |
| 36 | 12,42 | 12,96 | 13,05 |

These results show that any of the complexing agents listed above can be used for determination of niobium in the presence of tungsten. On the basis of the results obtained, the following experimental procedure is suggested.

Determination of niobium in the ternary alloy W–Si–Nb. 0.1 g of test material is placed in a platinum basin, and 2-3 ml of hydrofluoric acid is added; this is followed by nitric acid which is added slowly in order to avoid too vigorous a reaction; nitric acid is added until the alloy has dissolved completely. The contents of the basin are evaporated to dryness on a sand bath, and the dry residue fused with 2-3 g of potassium pyrosulfate. 30-40 ml of a 4% solution of oxalic acid, or ammonium oxalate or tartaric acid is added to the contents of the basin, and the mixture is heated on a sand bath and 30-40 ml of water then added; heating is continued until the melt has dissolved. The solution is transferred to a 250-300 ml beaker and the basin rinsed with cold water, the volume being made up in this way to 150-200 ml; 5 drops of hydrochloric acid (sp. gr. 1.19 is added, and the niobium is precipitated with 20-25 ml of a 3% aqueous solution of cupferron. Cupferron is added slowly with continuous stirring of the solution. A small amount of macerated paper is added and the solution carefully stirred until the precipitate has coagulated completely. The precipitate is filtered through a 7-9 cm diameter filter paper (white band) and washed 6-8 times with cold water containing 20 ml of the 3% aqueous solution of cupferron and 1 ml of concentrated hydrochloric acid per liter; the precipitate is thereby transferred quantitatively onto the filter paper. Filter paper plus precipitate are then returned to the basin in which it is ashed, and then calcined in a muffle at 500-600° until the carbon on the paper has been burnt off completely. The residue is fused with 1-2 g of potassium pyrosulfate, according to the amount of the residue, fusion being carried out over a small flame; 20-30 ml of 4% oxalic acid is added to the contents of the basin and the whole heated, 20-30 ml of water is then added and heating continued until the melt has dissolved; the contents of the basin are transferred to a beaker, 5 drops of hydrochloric acid is added and reprecipitation carried out as described above. Filter paper and precipitate are placed in a tared platinum or porcelain crucible in which they are then ashed; the ash is calcined for 15-20 minutes at 1000°, and then allowed to cool in a desiccator and finally weighed as niobium pentoxide. The conversion factor from $Nb_2O_5$ to Nb is 0.6990.

Results for the determination of niobium in this alloy are given in Table 2.

Tungsten can be determined in the filtrate after removal of the niobium. For this purpose, both the filtrates are combined and the oxalic acid destroyed, and, where necessary, the cupferron also; tungsten is then determined by one of the known methods.

In order to check on the completeness of the separation of niobium from tungsten, we examined the separated precipitate of niobium pentoxide for its tungsten content, using the radioactive indicator $W^{185}$ for this purpose.

To a dissolved aliquot (0.1 g) of the ternary alloy W–Si–Nb was added an active solution containing the radioactive isotope of tungsten $W^{185}$ with a known specific activity. All the operations enumerated in the technique described above were then repeated. The calcined and weighed residue of niobium pentoxide was fused with 1-2 g of potassium pyrosulfate, and the melt obtained dissolved in 15 ml of 4% oxalic acid in a 25 ml standard flask; the volume of this solution was made up to the mark with water. 0.2 ml of this solution was placed on an aluminum plate, and, after drying, the activity was measured on a B torsion counter. From this activity it was then possible to assess the amount of tungsten which had been coprecipitated with the niobium pentoxide. Results of these experiments are given in Table 3.

TABLE 3

Examination of the Isolated Residues of Niobium Pentoxide for their Content of Tungsten by means of the Radioactive Tungsten Isotope $W^{185}$

| Test material | Amount taken, in mg | | Activity of the original solution, in impulses/minute | Niobium pentoxide residue activity after tungsten separation | Amount of W found in the niobium residue, in mg |
|---|---|---|---|---|---|
| | Nb | W | | | |
| Standard solution | 4,48 | 60 | 1 095 200 | Background | 0,0 |
| | 4,48 | 100 | 1 095 200 | Background | 0,0 |
| | 8,96 | 160 | 1 095 200 | 2375 | 0,2 |
| | 8,96 | 00 | 1 095 200 | Background | 0,0 |
| Alloy | 12,96 | 70 | 1 105 400 | 1375 | 0,1 |
| | 13,05 | 70 | 1 249 200 | 3000 | 0,2 |
| | 42,75 | 40 | 1 105 400 | 8875 | 0,8 |
| | 34,16 | 55 | 1 157 100 | 20 250 | 1,7 |

By means of this experiment it was established that the amount of tungsten trapped by the niobium precipitate depends on the amount of the latter. During precipitation of 5 and 10 mg of niobium in the presence of 100 mg of tungsten, the niobium pentoxide obtained was found to be pure, and did not contain any tungsten.

During the examination of the niobium pentoxide residues obtained from the alloys, it was observed that coprecipitation of tungsten commences at niobium contents in excess of 30%.

Determination of niobium in steels containing tungsten. During the determination of niobium in steels and other materials containing, in addition to tungsten, other elements such as iron, titanium, vanadium and elements which are also precipitated by cupferron, it is recommended that niobium be precipitated beforehand with tannin in the presence of ascorbic acid, according to a method which we have developed previously [5].

1-2 g of steel is dissolved by boiling the sample with 20-25 ml of hydrochloric acid (1 : 1) in a 300 ml beaker. 5 ml of nitric acid(sp. gr. 1.40)is then added in order to oxidize the elements, boiling is continued and the solution evaporated almost to dryness. 30 ml of hydrochloric acid (1 : 2) is added and the whole boiled until complete removal of nitrogen oxides. If, during the boiling operation, the volume of the solution should decrease by 1/3, then 10-20 ml of water is added so as to preserve the requisite hydrochloric acid concentration. The solution is diluted with water to 180-190 ml, and, without paying attention to the occasional presence of a light-black precipitate, 1-2 g of ammonium chloride is added, followed by 0.1-0.2 g of ascorbic acid, and the whole is heated to the boil. To the hot solution is added (dropwise) 10 ml of a freshly prepared 1% aqueous solution of tannin (tannin dissolves in hot water) with continuous stirring. Tungsten is thereby coprecipitated. The solution is kept at the boiling point for 2-3 hours until the precipitate has coagulated completely; a small amount of macerated paper is added, and, after the solution has cooled (it can be left overnight) the precipitate is filtered through a 7-9 cm filter paper (white band), and then washed 6-8 times

with a cold 4% solution of hydrochloric acid. Filter paper plus precipitate are placed in a platinum crucible and ashed, crucible and contents are then heated in a muffle at 500-600° until all the organic materials have been burnt off. The residue is moistened with water and 2-3 ml of sulfuric acid (1 : 1) and 2-3 ml of hydrofluoric acid added; the crucible is placed on a sand bath and heated, gently at first, until the precipitate has dissolved, it is then heated more strongly until white fumes of sulfur dioxide appear. After the sulfur dioxide fumes have been coming off for 10 minutes, the crucible is cooled and 1-2 ml of water added, and the evaporation is repeated until no more than 2-3 drops of sulfuric acid remain in the crucible (evaporation to dryness must be avoided). Silica is removed in this way, and any particles remaining undissolved after treating the steel with hydrochloric and nitric acids are broken down completely. On cooling, 10 ml of hydrochloric acid (1 : 1) is added to the contents of the crucible and the whole heated until the salts dissolve. The solution is transferred to a 100 ml beaker and the crucible rinsed out several times with cold water, 0.05-0.1 g of ascorbic acid is added and the solution diluted with water to 80-90 ml; the solution is then heated to the boil and the niobium reprecipitated with tannin as described above.

The precipitate is ignited in a platinum basin and fused with 1-2 g of potassium pyrosulfate; 10-20 ml of 4% oxalic acid is added to the contents of the basin and the mixture heated until the melt has dissolved, niobium is then determined by the method described above for the determination of niobium in tungsten alloys.

## SUMMARY

A rapid and accurate method is suggested for the determination of niobium in the presence of large amounts of tungsten. In contrast to existing methods, this method is highly accurate and does not require the preliminary separation of niobium and tungsten. The method is based on the precipitation of niobium with cupferron in a weakly hydrochloric acid medium in the presence of oxalic acid which forms a complex compound with tungsten.

## LITERATURE CITED

[1] Yu. A. Chernikhov and V. G. Goryushina, Industrial Labs. 12, 517 (1946).

[2] W. R. Schoeller, A. R. Powell, and C. Jahn, Analyst 60, 506 (1935).

[3] R. B. Golubtsova, J. Anal. Chem. 6, 357 (1951).

[4] L. M. Budanova and K. D. Gavrilova, Industrial Labs. 15, 7 (1949).

[5] A. I. Ponomarev and A. Ya. Sheskol'skaya, J. Anal. Chem. 12, 355 (1957).*

Received March 8, 1958

*Original Russian pagination. See C.B. Translation.

# A NEW LUMINESCENT METHOD OF MICROCHEMICAL ANALYSIS (CRYSTALLOPHOSPHOR). COMMUNICATION 1. DETECTION OF ANTIMONY

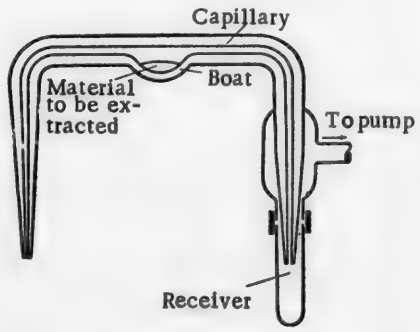
K. P. Stolyarov and N. I. Grigor'ev

The A. A. Zhdanov Leningrad State University

The exceptionally high sensitivity of luminescent reactions which makes it possible to work with micro- and ultramicro amounts of material ($10^{-12}$ – $10^{-15}$ g) permits their use in microchemistry. Only microcrystalloscopic, and to some extent spot (catalytic), reactions can compete with luminescent reactions.

The basic aim of our work was to develop new luminescent reactions based on the preparation of crystallophosphors, and to develop microchemical methods using these crystallophosphors.

Spot and microcrystalloscopic luminescent analysis do not differ from the usual microchemical analysis from the point of view of the techniques used for carrying them out. The ultraviolet source used was a PRK-4 mercury-quartz lamp. A capillary with an internal diameter of 0.1 mm for its drawn-out tip was used for sampling a few thousandths of a ml. For working with larger volumes, a micro test tube with a capacity of 0.1-0.2 ml was used. Removal of precipitates was carried out by filtration and centrifuging. The first technique was used during work on object glasses, the second technique being more suitable for work with capillaries and micro test tubes. We constructed a centrifuge capable of 6000 revolutions/minute for removing precipitates by centrifuging. The centrifuge consisted of a small motor, and an ebonite disc with horizontal sockets, and a guard ring. When such a centrifuge was used, 5-10 seconds was sufficient for removing crystalline precipitates.




Detection of antimonyon calcined calcium oxide. The reaction is based on the formation of a crystallophosphor CaO · Sb, which on being irradiated with ultraviolet light shines with a yellow-green color.

In order to prepare the calcium oxide, chemically pure calcium carbonate is calcined in a muffle and then triturated with water until a thick paste is obtained. The paste contained in a basin is placed in a desiccator on the floor of which water is poured. Using a platinum or nichrome loop, a drop of this paste is taken and calcined in a burner flame. The calcium oxide thus prepared is cooled and checked for purity by subjecting it to the action of ultraviolet radiation. The "pearl" formed should be colored a universal red. If there should be any luminescence this indicated that the original calcium carbonate is not pure enough. Such calcium carbonate should not be used, otherwise incorrect results will be obtained. When a sufficiently pure bead has been obtained, a drop of test solution containing the smallest possible amount of acid to keep the antimony in solution, is placed on it. The calcium oxide bead is then calcined again in such a way that the place on which the test solution has been placed is turned towards the side of the flame, and the bead examined again in the ultraviolet light. When antimony is present a luminescence is observed, the color of which changes with the antimony concentration; when fairly large amounts of antimony are present the color is greenish-yellow,

while when small amounts are present the color is a whitish-yellow (Table 1).

The sensitivity of this reaction, as shown in Table 1, is characterized by a limit of identification equal to 0.000001 $\gamma$ of antimony at a limiting dilution of $1:10^{10}$.

Bismuth, lead, uni- and divalent mercury, thallium, molybdenum, selenium, tellurium, and tungsten also form crystallophosphors with calcium oxide. Their basic characteristics are given in Table 2. Detection

TABLE 1

Color and Intensity of the Illumination of CaO · Sb Phosphors as a Function of the Antimony Content

| Sb content ($\gamma$) of a 0.01 ml drop | Color of the luminescence | Intensity of the illumination |
|---|---|---|
| 81.5 | Greenish-yellow | Bright |
| 8.15 | Greenish-yellow | Bright |
| 0.815 | Greenish-yellow | Bright |
| 0.081 | | |
| 0.008 | | Gradual decrease |
| 0.001 | Gradual transition | in intensity |
| 0.0001 | | |
| 0.00001 | | |
| 0.000001 | Pale-yellow | Weak |

TABLE 2

Formation of Crystallophosphors Based on CaO

| Activator | Color of the luminescence | Limit of identification ($\gamma$) in a drop of 0.01 ml | Limiting dilution | Activator | Color of the luminescence | Limit of identification ($\gamma$) in a drop of 0.01 ml | Limiting dilution |
|---|---|---|---|---|---|---|---|
| $Bi^{3+}$ | Blue-violet | 0,02 | $1;10^6$ | $Tl^{+}$ | Yellow-green | 0,02 | $1:5\cdot10^5$ |
| $Pb^{2+}$ | From bluish-white to lilac | 0,01 | $1:10^6$ | $Mo^{VI}$ | Turquoise | 67,0 | 1:150 |
| $Hg_2^{2+}$ | From yellow to blue-white | 0,02 | $1:5\cdot10^5$ | $Se^{2-}$ | Red | 0,04 | $1:10^6$ |
| $Hg^{2+}$ | From yellow to blue-white | 0,002 | $1:5\cdot10^6$ | $Te^{2-}$ | Red | 0,04 | $2:10^6$ |
| | | | | $W^{VI}$ | Rose-red | 100,0 | 1:100 |

of antimony in the presence of these elements is only possible when the absolute content of these materials in the drop of test solution does not exceed a certain maximum amount. These numerical amounts are given in Table 3.

Manganese, cobalt, nickel, copper, trivalent chromium, and iron do not form crystallophosphors with CaO, but strongly interfere with the detection of antimony by extinguishing, or strongly weakening, the luminescence which develops. The limiting ratios for these elements during the detection of trivalent antimony in a 0.01 ml drop are as follows:

Sb : Mn = 1 : 300000 at $10^{-4}$ and $10^{-5}$ $\gamma$ Sb
Sb : Co = 1 : 300000 at $10^{-4}$ $\gamma$ Sb
Sb : Ni = 1 : 3000000 at $10^{-4}$ and $10^{-5}$ $\gamma$ Sb
Sb : Cu = 1 : 200 at 0.815 $\gamma$ Sb
Sb : Cu = 1 : 1500 at 0.01 $\gamma$ Sb
Sb : Cu = 1 : 150000 at $10^{-5}$ $\gamma$ Sb
Sb : Cr = 1 : 30 at 0.815 $\gamma$ Sb

Sb : Cr = 1 : 300 at 0.008 γ Sb.
Sb : Cr = 1 : 2600 at $10^{-3}$ and $10^{-4}$ γ Sb
Sb : Fe = 1 : 75 at 0.815 γ Sb
Sb : Fe = 1 : 800 at 0.008 γ Sb
Sb : Fe = 1 : 60000 at $10^{-4}$ and $10^{-5}$ γ Sb

Detection of antimony by means of potassium ferrocyanide. Detection of antimony by means of $K_4Fe(CN)_6$ is carried out by a microscrystalloscopic reaction in filtered ultraviolet light. The order in which the individual operations are carried out has a considerable effect on the sensitivity of this reaction.

A drop of reagent solution and a drop of test solution are placed on an object glass; the drops are mixed. By drying the liquid slowly, well-formed crystals which strongly absorb ultraviolet radiation separate out. As long as the deposit remains damp, no illumination is observed. As the deposit dries out, a beautiful luminescence with a yellow color and which is very intense at high concentrations, develops. Excitation of the light occurs under the influence of ultraviolet radiation with $\lambda > 313$ mμ. It is the crystal edges which luminesce most.

The reaction can be speeded up as follows: drops of reagent and test solution are placed on a quartz object glass and the mixture dried rapidly. The reaction can be carried out quite well with amounts of antimony not less than 1.0 γ in a drop of 0.01 ml.

TABLE 3

Detection of Antimony in the Presence of Elements which Form Similar Crystallophosphors with CaO

| Element | $Pb^{2+}$ | $Hg^{2+}$ | $Hg^{2+}$ | Te, Se | $Mo^{VI}$ | $W^{VI}$ |
|---|---|---|---|---|---|---|
| Absolute content (γ) in a 0.01 ml drop | Less than 0.00104 | Less than 0.00002 | Less than 0.00002 | Less than 0.0025 | Less than 60.0 | Less than 100.0 |
| Absolute content of Sb (γ) in a 0.01 ml drop | $10^{-5}$ | $10^{-5}$ | $10^{-5}$ | $10^{-5}$ | $10^{-5}$ | $10^{-5}$ |

The sensitivity of the reaction can be increased by placing a drop of the reagent on an object glass and drying it out; a drop of test solution is then placed on the still hot dry spot formed by the reagent and this allowed to dry out freely. When this sequence of operations is followed, the sensitivity can be increased by approximately 1000 times. Data on the color and illumination intensity of the crystallophosphor $K_4[Fe(CN)_6]$ · ·Sb as a function of the $Sb^{3+}$ content is given in Table 4. It follows from these results that the sensitivity of the given reaction is characterized by a limit of identification of 0.001 γ of antimony ions at a limiting dilution of $1 : 10^7$.

Only arsenic ions give a similar reaction (limit of identification for arsenic ions, 0.12 γ at a limiting dilution of $1 : 8.3 \times 10^4$). Since many elements form precipitates with $K_4[Fe(CN)_6]$, it is necessary to separate most of the elements in order to carry out the above reaction successfully. Such a separation can be effected by extraction antimony from hydrochloric acid solutions with diethyl ether.

The limiting ratios of antimony to tin, germanium, and copper at which it is still possible to detect trivalent antimony without separating it from these elements are as follows:

Sb : Sn = 1 : 280 at 0.08 γ Sb
Sb : Sn = 1 : 2800 at $10^{-3}$ γ Sb
Sb : Ge = 1 : 120 at 0.008 γ Sb
Sb : Cu = 1 : 1 at 8.15 γ Sb

Decomposition of antimony ores and alloys and separation of antimony from accompanying elements. Breakdown of ores by fusion with sodium carbonate and sulfur. 3-5 mg of test material is placed in a No. 1 porcelain crucible and five times its amount of a 1:1 mixture of sodium carbonate and sulfur added, and the whole mixed thoroughly. A fine layer of the soda-sulfur mixture is strewn on top and the crucible covered with a lid; it is then uniformly heated from below, after 2-3 minutes the flame temperature is increased, and finally the crucible is heated until all the sulfur has been burnt off. After the melt has cooled it is leached with

TABLE 4

Color and Intensity of the Illumination of $K_4Fe(CN)_6 \cdot Sb$ Phosphors as a Function of the Antimony Content

| Antimony content ($\gamma$) in a 0.01 ml drop | Color of the luminescence | Intensity |
|---|---|---|
| 81.5 | Bright yellow | Strong |
| 8.15 | Bright yellow | Strong |
| 0.815 | Gradual appearance of a yel- | Decreasing intensity |
| 0.081 | low-green and bluish | of illumination |
| 0.008 | luminescence | |
| 0.001 | Yellow, blue in spots | Quite distinct |

water. 0.1-0.2 ml of the solution plus precipitate is taken and centrifuged. Centrifugate and wash liquors are transferred to a micro test tube; acetic acid is added, followed by 1-2 drops of a saturated solution of tin chloride (for removing arsenic) and 4-5 drops of concentrated hydrochloric acid. The mixture is heated on a water bath. The insoluble residue is centrifuged, and the antimony extracted from solution by extraction (see below).

Decomposition of oxide rocks. 3-5 mg of sample is placed in a micro crucible and 8-10 drops of a saturated solution of Rochelle salt added. The precipitate is brought into suspension and then heated. Boiling is stopped 7 minutes after the mixture has come to the boil. 0.1-0.2 ml of the solution with the precipitate suspended in it is taken and centrifuged. The precipitate is washed with 3-5 drops of water containing Rochelle salt, and the mixture centrifuged again; this centrifugate is then combined with the previous one. The solution obtained is acidified with hydrochloric acid, and the walls of the micro test tube rubbed gently with a glass rod. After some time a copious precipitate of potassium bitartrate is formed; antimony is precipitated with this as the oxychloride. The precipitate is filtered off and dissolved in the smallest possible amount of 6N HCl, and the antimony extracted. If the solution contains arsenic or trivalent iron, then $SnCl_2$ and fuming hydrochloric acid are added to the solution, the whole is heated, and the precipitate centrifuged.

Decomposition of alloys. 3-5 mg of sample is placed in a micro crucible and mixed with 5-10 times its amount of a mixture of $NH_4Cl$ and $NH_4NO_3$ (2:1); the whole is then heated until the sample has almost broken down completely. The melt obtained is dissolved in water strongly acidified with hydrochloric acid, and the solution centrifuged. A small aliquot of the centrifugate is taken and its iron content determined; if the iron content is low then 2-3 drops of 0.5 M ferric chloride solution is added. The solution is heated and excess ammonia added; the ferric hydroxide precipitate formed traps all the antimony from the solution. This precipitate is separated by centrifugation and dissolved in 1-2 drops of a solution of $SnCl_2$ in concentrated HCl. The antimony is extracted from the centrifugate by means of diethyl ether.

Extraction. Only 66% of the antimony passes into the ether layer when extraction is carried out once. Seven extractions are necessary to extract 99.95% of the antimony. When only a small amount of liquid is to be extracted it is best to carry out extraction in a continuous flow of liquid. For this purpose we used the extractor shown in the diagram. The material to be extracted is placed in the boat of the extractor in such an amount that its wetting edges are slightly lower than the opening of the capillaries. Suction is applied by means of a syringe with a screw-feed piston. Extraction is carried out by dipping the drawn-out tip of the

extractor in a vessel of ether, and the ether gradually sucked up. Subsequently, when the boat has been loaded, the ether is sucked through in small portions. As the ether accumulates in the receiver, the ether is distilled off by placing the receiver in a beaker with hot water and air sucked through. Using this technique evaporation proceeds without bumping. For greatest efficiency of extraction the solution should be 6N with respect to HCl.

These luminescent reactions which have been suggested for the detection of antimony have been tried out on pure salts, sulfide rocks, dolomite rocks, on bronze-type alloys, and also on pure antimony metal. The antimony content varied from 0.001 to 3.0% (with the exception of antimony metal). All tests gave uniformly positive results.

## SUMMARY

A technique is described for carrying out luminescent microchemical analysis, which is based on the formation of crystallophosphors.

New luminescent reactions for the microchemical detection of antimony are described which are based on the formation of the crystallophosphors CaO · Sb and $K_4[Fe(CN)_6]$ · Sb.

The possibility has been demonstrated of using the reactions described above for the qualitative analysis of mineral raw materials and alloys.

Received November 14, 1957

# DETERMINATION OF SMALL AMOUNTS OF LEAD IN ROCKS

Z. A. Baskova

The All-Union Scientific-Research Geological Institute, Leningrad

The analytical determination of small amounts of lead consists of the following three successive operations: 1) decomposition of the sample, 2) concentration of the lead, and 3) its final determination in a small volume of solution prepared by some technique or other. In choosing a method for breaking down the sample, it is important to bear in mind that lead may be present in the crystalline lattice of silicates, so that the decomposition of the sample should be as complete as possible. It is usually recommended that the sample be broken down with hydrofluoric acid mixed with sulfuric, perchloric, or nitric acid. Fusion of the sample with various fusion mixtures, or distillation of the lead by heating with a reducing agent, are techniques which are less often used.

Concentration of lead can be effected by variants of the method of extraction by coprecipitation with various collectors, or by extraction of certain inner-complex compounds of lead by organic solvents, or by electrolysis methods; sometimes a combination of these methods is expedient. Thus, lead has been coprecipitated with silver sulfide [1], strontium sulfate [2], barium sulfate [3], barium chromate [4], and with the fluorides of the rare earths and calcium [5]. In the extraction methods, use is made of the solubility of the compound of lead with diphenylthiocarbazone (dithizone) in chloroform or carbon tetrachloride [6]. This method has been recommended by several authors for the extraction of lead during the analysis of rocks [7, 8]. The compound of lead with sodium diethyldithiocarbamate has been suggested for separating lead from foodstuffs [9, 10].

Of other methods for separating lead, mention should be made of the distillation of lead by heating in a current of hydrogen [11], and in a vacuum in the presence of carbon [5, 16].

Whatever methods are used for breaking down the sample and for concentrating the lead, particular attention must be given to the possibility of loss of some of the lead by adsorption on the vessel walls and filter paper, and, on the other hand, to the possibility of the introduction of traces of lead with the reagents, most of which contain very small amounts of lead, and require careful purification [2, 7]. Reagents should be stored in quartz flasks or in flasks made from polyethylene or fluoro plastics. In all cases, blanks must be carried out so as to apply the necessary corrections to the experimental results.

Lead can be finally determined with satisfactory accuracy either photometrically or polarographically. Of the photometric methods, mention can be made of the sulfide [13], tetramethyldiphenylmethane [7], rubeanate [14], and dithizone methods. The dithizone method is the most sensitive; in addition, this method combines the extraction of lead dithizonate with its determination [7].

Polarographic determination of lead in a concentrate permits small contents of lead to be determined with high accuracy. Metals whose half-wave potentials coincide, or are similar to that of the lead, interfere with the polarographic determination of lead. Removal of interfering elements is partially achieved during the concentration stage, and can also be partially achieved by complexing these elements [12].

We have investigated the following methods of concentrating lead from the point of view of their application to the analysis of rocks:

1) Extraction of lead dithizonate with chloroform or carbon tetrachloride from an ammoniacal citrate solution, obtained directly after decomposition of a sample with hydrofluoric acid mixed with nitric or perchloric acid.

2) Extraction of lead from solution, based on its coprecipitation with mercuric sulfide or zinc sulfide.

3) Extraction of lead from solution, based on its coprecipitation with barium sulfate, with subsequent final separation of lead by extraction of lead dithizonate with an organic solvent.

4) Extraction of lead diethyldithiocarbamate with a mixture of pentanol and toluene.

5) Heating a mixture of the sample mixed with carbon in a vacuum, or in a stream of nitrogen in order to distill off the lead.

The percentage extraction of the lead was followed in most instances radiochemically.

Lead was finally determined polarographically, and by photometric determinations of solutions of the dithizonate extract.

For the polarographic determination of lead in rocks at the level of some thousandths of a percent, 1-2 g of sample was taken. The volume of the solution polarographed was 3-5 ml. The supporting electrolyte in most cases was a 0.1 N solution of potassium nitrate and nitric acid. The cathode was a dropping mercury electrode, while the anode was a saturated calomel electrode. Electrolytically prepared hydrogen was passed through the solution prior to polarograms being taken.

Colorimetric determination of lead was carried out on 0.1-0.2 g of sample

1. Separation of lead by extraction of lead dithizonate. An aliquot of the rock was broken down with a mixture of hydrofluoric and perchloric or nitric acids. A radioactive indicator (RaD) was added to the solution. After removal of the acids, the residue was dissolved on heating in dilute hydrochloric acid. To this solution was added 25 ml (30-40%) of an aqueous solution of ammonium citrate. The pH was adjusted to 8.5-10 by addition of ammonia. Lead was extracted with this solution by shaking the latter with several portions of a 0.01-0.02% solution of dithizone in chloroform, until the layer of the latter had a green color. The solution of the dithizonates was washed free of traces of ammonia solution by means of twice-distilled water. Lead was re-extracted from the organic solvent by shaking the latter with dilute nitric acid (0.02 N). The nitric solution was freed from traces of dithizone by shaking it with chloroform. The chloroform was discarded and the nitric acid solution evaporated to dryness. The activity of the residue obtained was then determined; the residue was dissolved in the supporting electrolyte and the lead content of the concentrate determined polarographically.

As experiment showed, the percentage extraction of lead by the method outlined above was, on an average, 91%.

Quantitative determination of lead isolated by the method indicated above from aliquots of 0.1-0.2 g was carried out photometrically.

2. Separation of lead by coprecipitation with sulfides. a) Coprecipitation with mercuric sulfide. Mercuric sulfide is a suitable collector because it is easy to remove the mercury from the concentrate obtained, by heating the latter. Mercuric nitrate (sufficient to give about 0.1 g of mercury) was added to the solution prepared in the appropriate way. Mercuric sulfide was then precipitated from the hydrochloric acid solution (0.4 N) by hydrogen sulfide. The solution plus precipitate was allowed to stand overnight, it was then filtered off, washed with hydrogen sulfide water, and ashed; the precipitate was heated to remove the mercury. The residue in the crucible was dissolved in dilute nitric acid.

Lead was finally separated by extracting it with a chloroform solution of dithizone from an ammoniacal citrate solution. The lead content of the concentrate was determined polarographically.

Experiments showed that 60-70% of the lead present is extracted when this technique is used.

b) Coprecipitation with zinc sulfide. Zinc (in the form of a zinc chloride solution) corresponding to 25-30 mg (on a metal basis) was added to the solution prepared in the appropriate way; the solution was then made weakly acid with respect to acetic acid (about 1%) and the zinc precipitated as sulfide with hydrogen

sulfide; the lead was thereby coprecipitated with it. 1 ml of a 1% gelatine solution was added to improve coagulation of the precipitate. After standing overnight the precipitate was filtered off, washed with hydrogen sulfide water, and dissolved in hot 2 N hydrochloric acid. Lead was finally determined polarographically; the supporting electrolyte used was hydrochloric acid, or a solution of potassium chloride in hydrochloric acid.

Experiments showed that about 80-90% of the lead can be coprecipitated with zinc sulfide under the conditions we used.

3. Separation of lead by coprecipitation with barium sulfate. Coprecipitation of lead was carried out under the conditions recommended by Starik [3].

Alcohol was added to depress the solubility of the lead sulfate. Starik carried out a final separation of lead from the precipitated sulfates by an electrolytic method. Our experiments showed that very small amounts of lead are more conveniently separated by extraction of lead dithizonate with chloroform.

A sample of rock was broken down with hydrofluoric acid. After decomposition of the sample, a standard solution of RaD was added to it; this was followed by 1-2 ml of 0.1 N barium chloride and concentrated sulfuric acid. The mixture was heated to remove traces of hydrogen fluoride. The residue was dissolved in boiling water acidified with hydrochloric acid. The solution was diluted with an equal volume of ethanol and allowed to stand overnight. The precipitated sulfates were filtered off and washed, and, after ashing, fused with sodium carbonate. The melt was leached with water, and the precipitated carbonates filtered off and carefully washed. The washed precipitate was dissolved in dilute nitric acid. To the acid solution was added 5-10 ml of a 25% solution of ammonium citrate, formed by ammonia until the blue color of thymol blue indicator appeared; a 0.02% solution of dithizone in chloroform was finally added.

To the alkaline filtrate was added 3-5 ml of ammonium citrate followed by nitric or hydrochloric acid until the greenish color of the thymol blue indicator appeared. A 0.002% solution of dithizone in chloroform was used for extracting the lead.

The extracts of lead dithizonate from both solutions were combined and the lead then determined as indicated above.

Tests showed that an average of 76% of the lead can be extracted by this technique.

4. Extraction of lead by extraction as lead diethyldithiocarbamate. Sodium diethyldithiocarbamate has been recommended for the separation of lead during the analysis of foodstuffs [9].

We adopted this method for analyzing rocks, using the technique described for organic materials [10]. According to this method, a reagent containing sodium citrate, sodium bicarbonate, and sodium diethyldithiocarbamate is added to a weak hydrochloric acid test solution. Subsequently the lead diethyldithiocarbamate (together with the diethyldithiocarbamates of the other metals) is extracted with a mixture of equal volumes of pentanol and toluene at a pH of 7. The pentanol-toluene mixture readily dissolves the diethyldithiocarbamates of all the reacting metals, and allows one to avoid the formation of a precipitate of the diethyldithiocarbamates of other metals, in particular of iron, which are sparingly soluble in pentanol alone. Lead is reextracted from the organic solvent by means of dilute hydrochloric acid. The hydrochloric acid solution of lead is poured into an aqueous ammoniacal solution of dithizone containing potassium cyanide and sodium metabisulfite. On shaking this solution with carbon tetrachloride, lead dithizonate is extracted by the organic reagent and colors the latter red. The optical density of the extract obtained is measured on a photocolorimeter or on a spectrophotometer. The amount of lead is found by means of a calibration curve prepared by means of standard solutions prepared in the same way as the test solution.

In this way it is possible to separate lead from all elements which interfere with its photometric determination by means of dithizone (in particular from thallium, bismuth, and tin).

For determination of lead in rocks, a finely ground sample was decomposed with a mixture of hydrofluoric and perchloric acids. After removal of the acids, the residue was dissolved in dilute hydrochloric acid. To this solution was added 25 ml of a citrate-bicarbonate solution containing 5-10 mg of sodium diethyldithiocarbamate; this was followed after 15 minutes by 25 ml of a mixture of equal volumes of pentanol and toluene. After shaking for two minutes, the layers being allowed to separate, the lower layer was discarded. The organic layer was washed with 25 ml of twice-distilled water. The lead was extracted from the organic

solvent by shaking it twice with 10 ml of a dilute hydrochloric acid solution (1 : 10*). The hydrochloric acid solution was added to an ammoniacal cyanide solution containing dithizone. Lead dithizonate was extracted from this solution with carbon tetrachloride. The lead dithizonate solution was made up to a definite volume (15 ml), after which its optical density was determined on a photocolorimeter. A calibration curve was constructed using solutions of lead in 10 ml of HCl (1 : 10), these solutions being given the same treatment as the test solutions.

In order to assure ourselves of the actual specificity of the method, comparatively large amounts of thallium, bismuth, and tin (100-250 γ) were taken, and extractions carried out under the same conditions as those used for extracting lead. During the re-extraction with dilute hydrochloric acid, complete removal of the elements indicated was achieved.

Results for the determination of lead in rocks by the method just described, agree with the results obtained by the other methods (Table).

Comparative Results for the Determination of Lead by the Various Methods

| Sample | Lead found, in % | | | | |
|---|---|---|---|---|---|
| | Polarographically | | | Photometrically | |
| | After extraction with dithizone solution | After coprecipitation with $BaSO_4$ | After heating in the presence of carbon | After extraction with dithizone solution | After extraction as diethyldithiocarbamate |
| Granodiorite | $1,5 \cdot 10^{-3}$ | $1,6 \cdot 10^{-3}$ | $1,6 \cdot 10^{-3}$ | $1,7 \cdot 10^{-3}$ | $1,6 \cdot 10^{-3}$ |
| Even grained granodiorite | $1,6 \cdot 10^{-3}$ | $1,5 \cdot 10^{-3}$ | $1,6 \cdot 10^{-3}$ | $1,5 \cdot 10^{-3}$ | $1,6 \cdot 10^{-3}$ |
| Porphyry, Granite | $3,6 \cdot 10^{-3}$ | $3,1 \cdot 10^{-3}$ | $2,9 \cdot 10^{-3}$ | $3,8 \cdot 10^{-3}$ | $3,4 \cdot 10^{-3}$ |
| Quartz porphyry | $4,1 \cdot 10^{-3}$ | | $3,9 \cdot 10^{-3}$ | | |
| Triandesite | $2,1 \cdot 10^{-3}$ | $2,2 \cdot 10^{-3}$ | | $2,2 \cdot 10^{-3}$ | |
| Feldspar | $1,0 \cdot 10^{-3}$ | $1,0 \cdot 10^{-3}$ | | $1,0 \cdot 10^{-3}$ | |
| » » | $1,4 \cdot 10^{-3}$ | | $1,5 \cdot 10^{-3}$ | $1,7 \cdot 10^{-3}$ | $1,5 \cdot 10^{-3}$ |
| » » | $1,7 \cdot 10^{-3}$ | | | $1,8 \cdot 10^{-3}$ | $1,8 \cdot 10^{-3}$ |

Lead was extracted to the extent of 97%

5. Separation of lead by distillation. Separation of lead by distillation was carried out by heating the test sample in the presence of carbon in a vacuum** or in a nitrogen stream. The test sample, carefully ground with an equal amount by weight of carbon, was heated in a quartz tube. In the first experiment the lead was separated at a temperature of 1050-1100° and a pressure of $10^{-1} - 10^{-2}$ mm Hg, while in the second experiment lead was removed at a temperature of 1100-1150° in a stream of nitrogen. The distillate which condensed on the cooler parts of the tube was washed off with hot nitric acid (1 : 1); this solution was evaporated to dryness. The lead content of the concentrate thus obtained was determined polarographically. Distillation in vacuo took 3-4 hours, while in nitrogen, distillation was carried out for about 8 hours.

Experiments showed that using this technique it is possible to separate 80 to 100% of lead contained in the rock.

The table contains a comparison of the results obtained for the determination of lead in several samples when the various methods for the preliminary separation and final determination of lead were used.

## DISCUSSION OF RESULTS

From the experiments described above on the concentration of lead, the following conclusions can be drawn:

*This solution was prepared by diluting redistilled hydrochloric acid (1 : 1).

**After completing this work we learned that N. Iordanov and L. Kocheva had also carried out separation of lead in a vacuum in the presence of carbon, and with HgS [16].

1. Concentration, based on the direct extraction of lead dithizonate by means of chloroform from a solution obtained by decomposition of the sample, permits the extraction, on an average, of 91% of all the lead in the rock. This technique of concentration by extraction takes less time than those methods based on coprecipitation.

2. Concentration based on coprecipitation of lead with mercury and zinc sulfides does not achieve the desired results: only 60-70% is extracted with mercuric sulfide and 80-90% with zinc sulfide. The drawback of this method is the high degree of contamination of the concentrate – the sulfide precipitate, which acts as a carrier – by other elements present in solution. Finally, this method is coupled with difficulties arising from the possibility of the hydrolysis of certain salts in the weakly acid solutions, and the even greater complexity of the composition of the concentrate following upon this.

3. Extraction of lead by cocrystallization with the sulfates of the alkaline earth elements, coupled with a subsequent final separation of lead by extraction makes it possible to separate 76% of lead, on the average. The method is complicated by the number of operations involved (for example, fusion with soda, filtration), which lengthen the time taken to carry out a determination, and may cause loss of part of the lead.

4. Separation of lead by extraction of lead diethyldithiocarbamate, with subsequent extraction of lead from the organic solvent by means of dilute hydrochloric acid, ensures removal of lead from all the elements interfering with its final photometric determination with dithizone, in particular, from bismuth and thallium. Lead is extracted to the extent of 97%, on an average. It should be pointed out that an appreciable amount of the reagent employed does not require special preliminary purification. All things considered, this method allows one to separate and determine small amounts of lead contained in rocks fairly simply.

5. Concentration of the lead by distillation effected by heating with carbon permits extraction of 80-100% of the lead. The advantage of the method is the possibility of carrying out a comparatively rapid and simple separation of lead, even from comparatively large samples (2-10 g). The drawback of the method is the complexity of the apparatus.

6. Final photometric determination of lead in the form of its dithizonate is sensitive enough, and permits the lead content of the concentrates to be determined with satisfactory accuracy. The advantage of the method is the possibility of determining lead to relatively small samples; its drawback is the use of potassium cyanide.

The polarographic technique permits small amounts of lead, separated from fairly large samples (1-2 g), to be determined comparatively rapidly and with a high degree of accuracy. When this technique is used potassium cyanide can be avoided.

7. The choice of the method to be used for isolating and determining lead in each special case should be made on the basis of the characteristic composition of the test material and the amount of the latter available.

The author wishes to thank Yu. V. Morachevskii for his valuable advice in the course of the work described above.

## SUMMARY

Small amounts of lead in rocks have been determined after concentrating the lead by the following techniques: extraction of lead dithizonate or lead diethyldithiocarbamate with organic solvents; coprecipitation of lead sulfide with mercury or zinc sulfide; coprecipitation of lead sulfate with barium sulfate; distilling off the lead by heating the sample with a solid reducing agent (carbon) in a vacuum, or in a stream of nitrogen. The lead separated by these various techniques was finally determined either polarographically or colorimetrically (dithizone).

The advantages and disadvantages of the various methods for concentrating traces of lead are discussed.

## LITERATURE CITED

[1] G. Hevesy and R. Hobbie, Nature 128, 1038 (1931); Zeit. f. analyt. Chemie 88, 1 (1932).

[2] Rosenquist, Amer. J. Sci. 240, 359 (1940).

[3] I. E. Starik, "Radioactive Methods for the Determination of Geological Time" [in Russian] Izd. AN SSSR, Moscow, 1938, p. 87.

[4] I. E. Starik, In the Symposium "The Use of Labelled Atoms in Analytical Chemistry," [in Russian] 1955, p. 192.

[5] F. E. Starik,* "Bulletin of the Commission of the Determination of the Absolute Age of Geological Formations", AN SSSR, No. 1, p. 45, 1955.

[6] Fischer, Ann. 190, 118 (1878); 212, 316 (1882); Wiss. Veroffentlich Siemens-Konzern 4, 1958 (1925).

[7] E. Sandell, Ind. Eng. Chem. Anal. Ed. 2, 464 (1937); E.B. Sandell, "Colorimetric Determination of Traces of Metals," [Translated from English] Goskhimizdat, Moscow-Leningrad, 1949.

[8] G. R. Tilton, C. C. Patterson, H. C. Brown, M. G. Inghram, R. I. Hayden, D. C. Hess, and E. S. Larsen, Bull. of the geol. Soc. of Amer. 66, 1131 - 1148, (1955).

[9] S. L. Tompsett and A. B. Anderson, Biochem. J. 29, 1851 (1953).

[10] J. C. Cage, Analyst 80, No. 956 (1955); J. C. Cage, Analyst 82, No. 975 (1957).

[11] G. I. Novikov and N. I. Chaikina, Information Bureau VSEGEI**, No. 2 (1955).

[12] J. Heyrovsky, Techniques of Polarographic Analysis. Collection of Articles, Izd AN SSSR, 1951;*** K. S. Pakhomova and L. P. Volkova, Industrial Labs. 22, 283 (1956); R. Prishibl, "Complexones in Chemical Analysis," [Translated from Czech] IL, Moscow, 1955 [Author's name not verified].

[13] M. T. Golubeva, Hygiene and Sanitation, No. 5, 29 (1946).

[14] K. B. Yatsimirskii and F. D. Kashirina, Industrial Labs. 13, No. 1 (1952).

[15] Z. A. Baskova and G. I. Novikov, Geochemistry, No. 7, 580 (1957).

[16] N. Iodanov and L. Kocheva, Bull. Chem. Inst. Bulgarian Acad. Sci. 4, 327 (1956).****

Received January 2, 1958

*Translation of Russian — Publisher's note.

**All-Union Geological Scientific Research Institute.

***Russian translation.

****Probably Bulgarian. Transliteration of Russian — B"lg.

# AMPEROMETRIC TITRATION OF IRIDIUM USING A ROTATING PLATINUM ELECTRODE

N. K. Pshenitsyn and N. A. Ezerskaya

Institute of General and Inorganic Chemistry, Acad. Sci. USSR, Moscow

We established previously [1] that it is possible to obtain clearly defined current-voltage curves for $Na_2IrCl_6$ on a platinum electrode; this fact has permitted us to use these curves for the amperometric titration of iridium. The amperometric titration method is no less accurate and sensitive than the polarographic method, and is simpler than the latter, while the apparatus used is more readily available. Oxidation–reduction, and precipitation reactions can be used as a basis for amperometric titration. Since no reagents have hitherto been found which precipitate iridium completely enough, we only used the reduction of $Ir^{IV}$ as a basis for amperometric titration. Reactions of this type proceed quickly and the titration curves obtained have a clearly defined inflection at the equivalence point. Hydroquinone and ascorbic acid were chosen as the titrating reagents. These reducing agents have been successfully used by a number of workers [2-6] for the titrimetric determination of comparatively large amounts of iridium. Other reducing agents which have been described in the literature, such as $FeSO_4$, $K_4Fe(CH)_6$, KI and $TlCl_3$, cannot be used — the first and second, because trivalent iron is reduced at the potential at which iridium is titrated, and the last because of insufficient selectivity. Titration was carried out on the basis of the cathodic wave for the reduction of $Ir^{IV}$ at a potential corresponding to the limiting current. Titration on the basis of the anodic waves of hydroquinone or ascorbic acid is impossible, since, as titration proceeds, the trivalent iridium formed gives an oxidation wave [1] which fuses with the oxidation wave of hydroquinone or ascorbic acid.

Titration was carried out on the apparatus described in [1]. The indicator electrode was a rotating platinum electrode 5-7 mm long and 0.5 mm in diameter, while the reference electrode was a saturated calomel electrode. The electrode was rotated at the rate of 800-1000 revolutions/minute. Measurements were carried out by means of the SGM-8 "Geologorazvedka" polarograph with a galvanometer whose sensitivity was $2.32 \times 10^{-9}$ amps./mm/m. The titrant was added from a microburet with 0.02 ml scale divisions. The volume of the solution being titrated, during titration of tenths and hundredths of a milligram was 10 ml, while for the titration of milligram amounts of volume was 30 ml. The supporting electrolyte was 0.1 N NaCl. The $Na_2IrCl_6$ was prepared in the usual way; the solution was standardized gravimetrically; the concentrations used were approximately 1 mg/ml and 0.1 mg/ml. The solutions of hydroquinone and ascorbic acid used were approximately 0.025, 0.005, and 0.0005 N (1 ml of solution corresponded respectively to 5.0, 1.0, and 0.1 mg of iridium). Solutions of both reagents were prepared in twice-distilled water, 2 ml of HCl being added per ml of solution ; the solutions were stored in dark-colored flasks. Under these conditions the normality of the hydroquinone solutions remained constant over 2-3 weeks, while that of the ascorbic acid solutions was, unfortunately, only constant for 2-3 days. Stabilization of the ascorbic solutions by addition of formic acid and Complexon III, as carried out by other workers [7], was impossible in our case, since these compounds readily reduce $Ir^{IV}$ to $Ir^{III}$. Hydroquinone solutions were standardized visually by titration with dichromate (using diphenylamine as indicator). Ascorbic acid solutions were standardized by visual titration with trivalent iron (in the presence of $SCH^-$) or by amperometric titration with a standard solution of $Ir^{IV}$; standardization was carried out daily.

Titration of iridium with dichromate. In acid media, iridium is very rapidly reduced by hydroquinone at room temperature. Hydroquinone is not reduced on the rotating platinum electrode; on the contrary, it gives

an anodic oxidation wave with a limiting current starting at approximately +0.55 volt (saturated calomel electrode). Quadrivalent iridium gives a reduction wave with $E_{1/2}$ = +0.73 volt (Fig. 1). As a result of this, the amperometric curves obtained during the titration of quadrivalent iridium with hydroquinone over the range +0.4—0.5 volt have an L-shape. Changes in the pH of the solution over the range 0.3 to 3.0 do not affect the

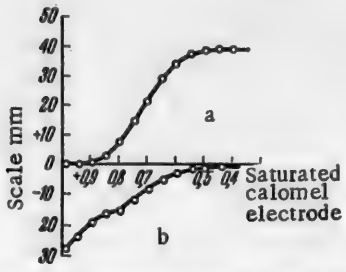



Fig. 1. Current-voltage curves for $Na_2IrCl_6$ and hydroquinone: a) $6 \times 10^{-4}$ M $Na_2IrCl_6$ in 0.1 N NaCl; b) $2.5 \times 10^{-4}$ M hydroquinone in 0.1 N NaCl.

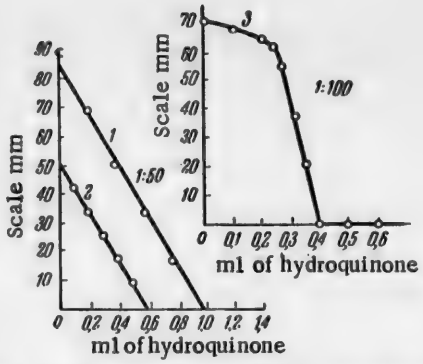



Fig. 2. Titration curves of $Ir^{IV}$ with hydroquinone: 1) 1 mg Ir ($5.2 \times 10^{-4}$ M); 2) 0.6 mg Ir ($3.1 \times 10^{-4}$ M); 3) 2 mg Ir ($1.4 \times 10^{-3}$ M). For curves 1 and 2, 1 ml of hydroquinone solution corresponds to 1 mg Ir, while for curve 3, 1 ml of hydroquinone corresponds to 5 mg Ir.

titration results. Titration was usually carried out in the presence of HCl (pH 1.5) in 0.1 N NaCl. Titration results for various amounts of iridium (from $1.5 \times 10^{-3}$ to $1 \times 10^{-5}$ M/liter) (Table 1) indicate that the determination can be carried out with satisfactory accuracy. The mean relative reproducibility of the results amounts to 1-2%. Titration curves for solutions containing $10^{-5} - 5 \times 10^{-4}$ M iridium are in the form of two intersecting straight lines, while titration curves for more concentrated solutions have an initial small horizontal section (Fig. 2).

Rhodium present in any amount does not interfere with the titration of iridium with hydroquinone, since rhodium is reduced on the platinum electrode at more negative potentials, and, moreover, it is not titrated by hydroquinone. For the same reason Pt, Pd, Cu, Ni, Se, and Te do not interfere. On the other hand, $Au^{III}$

TABLE 1

Titration of $Na_2IrCl_6$ with Hydroquinone

| Ir taken, mg | Ir concentration, mole/liter | Volume of solution, ml | Normality of hydroquinone solution, N | Ir found, mg | Absolute error, mg | Relative error, % |
|---|---|---|---|---|---|---|
| 8,57 | $1,5 \cdot 10^{-3}$ | 30 | 0,005 | 8,40 | —0,17 | —1,9 |
| 4,20 | $0,7 \cdot 10^{-3}$ | 30 | 0,005 | 4,27 | +0,070 | +1,6 |
| 2,14 | $1,1 \cdot 10^{-3}$ | 10 | 0,005 | 2,17 | +0,030 | +1,4 |
| 1,515 | $6,2 \cdot 10^{-4}$ | 10 | 0,005 | 1,525 | +0,010 | +0,7 |
| 0,918 | $4,7 \cdot 10^{-4}$ | 10 | 0,005 | 0,920 | +0,020 | +2,2 |
| 0,850 | $4,4 \cdot 10^{-4}$ | 10 | 0,005 | 0,870 | +0,020 | +2,3 |
| 0,500 | $2,6 \cdot 10^{-4}$ | 10 | 0,005 | 0,510 | +0,010 | +2,0 |
| 0,200 | $1,0 \cdot 10^{-4}$ | 10 | 0,005 | 0,200 | 0 | 0 |
| 0,095 | $4,6 \cdot 10^{-5}$ | 10 | 0,0005 | 0,094 | —0,001 | —1,0 |
| 0,060 | $3,1 \cdot 10^{-5}$ | 10 | 0,0005 | 0,059 | —0,001 | —1,6 |
| 0,050 | $2,6 \cdot 10^{-5}$ | 10 | 0,0005 | 0,049 | —0,001 | —2,0 |
| 0,035 | $1,8 \cdot 10^{-5}$ | 10 | 0,0005 | 0,038 | —0,003 | +8,5 |
| 0,020 | $1,0 \cdot 10^{-5}$ | 10 | 0,0005 | 0,020 | 0 | 0 |
| 0,015 | $7,7 \cdot 10^{-4}$ | 10 | 0,0005 | 0,018 | +0,003 | +20,0 |

whose half-wave potential is similar to that of $Ir^{IV}$ is also reduced by hydroquinone, and accordingly interferes with determination of iridium. In the presence of appreciable amounts of quadrivalent ruthenium, establish-

ment of the equivalence point from the titration curves is complicated by the fact that ruthenium is partially reduced by hydroquinone. After treating solutions containing $Ir^{IV}$ and $Ru^{IV}$ with aqua regia, and subsequent evaporation to dryness with hydrochloric acid in the presence of sodium chloride, ruthenium is converted into a compound which is not titrated by hydroquinone, but gives instead a considerable reduction current at +0.4 volt. By preparing the solutions in this way it is possible to determine iridium fairly accurately in the presence of as much as 20-25 times its amount of ruthenium. It should be noted that even small amounts of ruthenium interfere with the polarographic determination of iridium.

Determination of iridium in the presence of small amounts of iron is complicated by the fact that $Fe^{III}$ gives a reduction wave close to that of $Ir^{IV}$ on the platinum electrode. Interference from iron can, however, be overcome by addition of phosphoric acid. When this is done, iridium can be determined in the presence of even as much as 100 times its own amount of iron.

Results for the titration of iridium in the presence of various metals are given in Table 2.

TABLE 2

Titration of Iridium with Hydroquinone in the Presence of Other Metals

| Ir taken, mg | Ir : Me | Amount of metal, mg | | | | | | | | | Ir found, mg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pl | Pd | Rh | Ru | Cu | Ni | Fe | Se | Te | |
| 0,060 | 1:10 | — | — | 0,6 | — | — | — | — | — | — | 0,058 |
| 0,060 | 1:200 | — | — | 12,0 | — | — | — | — | — | — | 0,060 |
| 0,050 | 1:100 | — | 5,0 | — | — | — | — | — | — | — | 0,050 |
| 0,050 | 1:200 | — | 10,0 | — | — | — | — | — | — | — | 0,049 |
| 0,020 | 1:20 | 0,4 | — | — | — | — | — | — | — | — | 0,020 |
| 0,020 | 1:200 | 4,0 | — | — | — | — | — | — | — | — | 0,020 |
| 0,045 | ~1:1 | — | — | — | 0,05 | — | — | — | — | — | 0,046 |
| 0,045 | ~1:10 | — | — | — | 0,50 | — | — | — | — | — | Determination impossible |
| 0,060 | 1:2 | — | — | — | 0,12* | — | — | — | — | — | 0,060 |
| 0,060 | 1:20 | — | — | — | 1,20* | — | — | — | — | — | 0,062 |
| 0,060 | 1:50 | — | — | — | 3,00* | — | — | — | — | — | 0,070 |
| 0,060 | 1:20 | — | — | — | — | 1,2 | — | — | — | — | 0,059 |
| 0,060 | 1:10 | — | — | — | — | — | 0,6 | — | — | — | 0,061 |
| 0,050 | 1:1 | — | — | — | — | — | — | 0,05 | — | — | 0,050 |
| 0,050 | 1:10 | — | — | — | — | — | — | 0,50 | — | — | 0,057 |
| 0,060 | 1:60 | — | — | — | — | — | — | — | 3,0 | — | 0,063 |
| 0,050 | 1:100 | — | — | — | — | — | — | — | — | 5,0 | 0,052 |
| 0,60 | — | 2,0 | 0,5 | 6,0 | 3,0* | — | — | — | — | — | 0,60 |
| 0,60 | — | 3,0 | 0,5 | 3,0 | 1,5* | 2,0 | — | — | 0,3 | 0,5 | 0,61 |
| 0,80 | — | — | — | 7,0 | 3,0* | 5,0 | — | 0,5 | 3,0 | 2,0 | 0,78 |

*$Ru^{IV}$ solutions were treated with aqua regia and then twice evaporated to dryness with HCl in the presence of NaCl.

Titration of iridium with ascorbic acid. Reduction of $Ir^{IV}$ by ascorbic acid, as already established by Pshenitsyn and Prokof'eva [6], proceeds stoichiometrically at room temperature. Ascorbic acid is oxidized on the platinum electrode to give an anodic wave whose half-wave potential depends on the pH of the solution. At a pH of 1.5 the half-wave potential of ascorbic acid is approximately equal to 0.7-0.8 volt (saturated calomel electrode)(Fig. 3). The curves obtained during the amperometric titration of iridium with ascorbic acid at E = 0.4-0.5 volt (saturated calomel electrode) (Fig. 4) are similar in shape to those obtained during titration of iridium with hydroquinone (Fig. 2). Since the oxidation-reduction potential of ascorbic acid increases appreciably with increasing acidity of the medium, experiments were carried out on the titration of $Na_2IrCl_6$ at HCl concentrations ranging from $10^{-3}$ to 10 N. It was found that, on changing the acidity, the titration results did not change since the oxidation-reduction potential of $IrCl_6^{2-}/IrCl_6^{3-}$ also increase. Nevertheless, in a strongly acid medium (5-10 N HCl) the reduction of iridium was slowed down, and a titration took a very long time. Subsequent experiments were carried out at a pH of 1.5. Table 3 contains the results for the titration of various amounts of iridium with ascorbic acid.

The mean relative reproducibility during titration of hundredths of a milligram of iridium (> $10^{-5}$ M) is approximately 4%, while for the titration of tenths of a milligram of iridium (> $10^{-4}$ M) it is 2-3%. The relative experimental error varies from 1 to 5%, while for the titration of very small amounts (1 × $10^{-5}$ M and

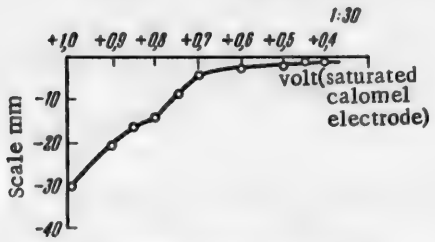



Fig. 3. Current-voltage curves for 2.5 × $10^{-4}$ M ascorbic acid. Supporting electrolyte 0.1 N NaCl, pH 1.5.

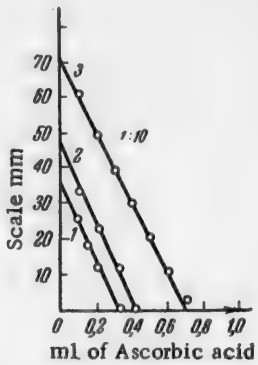



Fig. 4. Titration curves for iridium with ascorbic acid: 1) 0.03 mg Ir (1.5 × $10^{-5}$ M); 2) 0.4 mg Ir (2 × $10^{-5}$ M); 3) 0.07 mg Ir (3.6 × $10^{-5}$ M). (1 ml corresponds to 0.1 mg Ir).

less) it amounts to 10-15%. The smallest amount of iridium which can be determined when the volume of the solution is 10 ml is 0.02 mg. Those metals which do not interfere during titration of iridium with hydroquinone, do not interfere with titrations involving ascorbic acid as titrant. Gold, ruthenium, and iron interfere. For preventing interference from ruthenium, the same technique as that used for titration with hydroquinone was adopted. This technique permitted determination of iridium in the presence of as much as 50 times its amount of ruthenium. Gallai, Tiptsova, and Peshkova [7] during titration of $Ce^{IV}$ with ascorbic acid, established that as a consequence of the fact that there is hardly any reduction of $Fe^{III}$ by ascorbic acid in 2 N $H_2SO_4$, iron does not interfere with determination of cerium.

TABLE 3

Titration of $Na_2IrCl_6$ with Ascorbic Acid

| Ir taken, mg | Concentration, mole/liter | Ascorbic acid concentration, N | Ir found, mg. | Absolute error, mg | Relative error, % |
|---|---|---|---|---|---|
| 9,40 | $4,9 \cdot 10^{-3}$ | 0,025 *N* | 9,50 | +0,10 | +1,0 |
| 8,10 | $4,2 \cdot 10^{-3}$ | 0,025 *N* | 8,25 | +0,15 | +1,8 |
| 6,30 | $3,3 \cdot 10^{-3}$ | 0,025 *N* | 6,50 | +0,20 | +3,2 |
| 1,00 | $5,2 \cdot 10^{-4}$ | 0,005 *N* | 1,03 | +0,03 | +3,0 |
| 0,60 | $3,1 \cdot 10^{-4}$ | 0,005 *N* | 0,60 | 0 | 0 |
| 0,50 | $2,6 \cdot 10^{-4}$ | 0,005 *N* | 0,50 | 0 | 0 |
| 0,20 | $1,0 \cdot 10^{-4}$ | 0,005 *N* | 0,19 | −0,01 | −5,0 |
| 0,07 | $3,6 \cdot 10^{-5}$ | 0,0005*N* | 0,073 | +0,003 | +4,3 |
| 0,05 | $2,6 \cdot 10^{-5}$ | 0,0005*N* | 0,050 | 0 | 0 |
| 0,03 | $1,5 \cdot 10^{-5}$ | 0,0005*N* | 0,032 | +0,002 | +6,6 |
| 0,02 | $1,0 \cdot 10^{-5}$ | 0,0005*N* | 0,023 | +0,003 | +15,0 |

Since ascorbic acid reduces $Ir^{IV}$ even in very acid media, we tried to use this fact for the determination of iridium in the presence of iron. It is clear from the results given in Table 4 that when titration is carried out in 7-10 N HCl, iron present to the extent of 100 times the iridium does not interfere with the titration of the latter. In such acid media, however, titration is slowed down. Moreover, the diffusion current of iron only disappears completely in 10 N HCl. Accordingly, another method of preventing interference from $Fe^{III}$ – complexing it as a phosphate complex by addition of 2 ml of $H_3PO_4$ (60%) – is more convenient; when this technique is used the diffusion current of $Fe^{III}$ disappears completely, and, moreover, the rate of reduction of $Ir^{IV}$ is not slowed down.

TABLE 4

Titration of $Ir^{IV}$ in the Presence of $Fe^{III}$ at Various Acidities of the Medium (0.50 mg Ir was taken)

| Fe taken, mg | HCl concentration, N | Ir found, mg | Residual current, mm |
|---|---|---|---|
| 5.0 | $10^{-3}$ | 0.66 | 20 |
| 5.0 | 5 | 0.54 | 10 |
| 5.0 | 7 | 0.49 | 5 |
| 5.0 | 10 | 0.51 | — |
| 50.0 | 7 | 0.48 | 15.0 |

The results obtained (Table 5) indicate that it is possible to titrate $Ir^{IV}$ with ascorbic acid in the presence of Rh, Pt, Pd, Ru (for ratios of Ir: Ru not greater than 1:50), Cu, Ni, Pb, Se, Te, and Fe (after addition of $H_3PO_4$).

TABLE 5

Titration of Iridium with Ascorbic Acid in the Presence of Other Metals

| Ir taken, mg | Ir:Me | Amount of the other metal present as an impurity, mg | | | | | | | | | | Ir found, mg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pt | Pd | Rh | Ru* | Cu | Ni | Pb | Fe | Se | Te | |
| 0,50 | 1:10 | 5,0 | — | — | — | — | — | — | — | — | — | 0,52 |
| 0,50 | 1:100 | 50,0 | — | — | — | — | — | — | — | — | — | 0,51 |
| 0,60 | 1:10 | — | 6,0 | — | — | — | — | — | — | — | — | 0,62 |
| 0,60 | 1:100 | — | 60,0 | — | — | — | — | — | — | — | — | 0,62 |
| 0,60 | 1:10 | — | — | 6,0 | — | — | — | — | — | — | — | 0,60 |
| 0,60 | 1:100 | — | — | 60,0 | — | — | — | — | — | — | — | 0,62 |
| 0,50 | 1:10 | — | — | — | 5,0 | — | — | — | — | — | — | 0,51 |
| 0,50 | 1:90 | — | — | — | 45,0 | — | — | — | — | — | — | 0,49 |
| 0,50 | 1:20 | — | — | — | — | 10,0 | — | — | — | — | — | 0,50 |
| 0,50 | 1:20 | — | — | — | — | — | 10,0 | — | — | — | — | 0,52 |
| 0,50 | 1:20 | — | — | — | — | — | — | 10,0 | — | — | — | 0,50 |
| 0,066 | 1:10 | — | — | — | — | — | — | — | 0,6 | — | — | 0,066 |
| 0,066 | 1:100 | — | — | — | — | — | — | — | 6,0 | — | — | 0,066 |
| 0,40 | 1:25 | — | — | — | — | — | — | — | — | 10,0 | — | 0,41 |
| 0,40 | 1:25 | — | — | — | — | — | — | — | — | — | 10,0 | 0,40 |
| 0,70 | — | 3,0 | 3,0 | 7,0 | 7,0 | — | — | — | — | — | — | 0,73 |
| 0,80 | — | 3,0 | 3,0 | 5,0 | 3,0 | 10,0 | 3,0 | — | 5,0 | 1,0 | 0,5 | 0,84 |

*$Ru^{IV}$ solutions were treated with aqua regia and then twice evaporated to dryness with HCl in the presence of NaCl.


## SUMMARY

It has been established that it is possible to titrate small amounts of $Ir^{IV}$ ($10^{-5}$ – $10^{-3}$ M) amperometrically with hydroquinone and ascorbic acid respectively, in the presence of Rh, Pt, Pd, Cu, Ni, Pb, Se, and Te. Conditions have been found for the titration of iridium in the presence of $Ru^{IV}$ and $Fe^{III}$.


## LITERATURE CITED


[1] N. K. Pshenitsyn, N. A. Ezerskaya, and V. D. Ratnikova, J. Inorg. Chem. 3, 1791 (1958).

[2] D. I. Ryabchikov, Bull. Section on Platinum IONKh Acad. Sci. USSR 22, 35 (1948).

[3] W. Pollard, Bull. of Inst. Min. Met. 497, 9 (1948).

[4] N. K. Pshenitsyn and L. V. Prokof'eva, Bull. Section on Platinum IONKh, Acad. Sci. USSR 28, 229 (1954).

[5] A. Berka and J. Zyka, Chem. Listy 50, 829 (1956).

[6] N. K. Pshenitsyn and L. V. Prokof'eva, Bull. Section of Platinum IONKh, Acad. Sci. USSR 30, 176 (1955).

[7] Z. A. Gallai, V. G. Tiptsova, and V. M. Peshkova, J. Anal. Chem. 12, 469 (1957).*

Received December 19, 1957

*Original Russian pagination. See C.B. Translation.

# POTENTIOMETRIC DETERMINATION OF PHOSPHATE IONS

Z. I. Ivanova and P. N. Kovalenko

Rostov State University

The aim of the work described in the present article was to develop a rapid and accurate method for the potentiometric titration of phosphate ions.

We used a mercury electrode while the titrant used was a solution of mercuric nitrate; a saturated calomel half element was used as the reference electrode in the normal type of compensation setup. The indicator mercury electrode that was constructed had a number of advantages over mercury electrodes which have been suggested hitherto [1, 2]. The titration beaker 3 had an offshoot (Fig. 1), which was filled with mercury, and a tap 5 which served for pouring off the liquid which had been titrated and for washing the beaker. Contact was established by placing a platinum disc in the mercury, the platinum disc being connected via a wire fused into a glass tube provided with an external lead. The salt bridge was filled with a saturated solution of KCl or $KNO_3$.

The $Hg(NO_3)_2$ was added in small aliquots, and, towards the equivalence point, in drops.

Potentiometer readings were made every minute (after a constant value of the potential had been reached). A titration curve for phosphates is shown in Fig. 2.

TABLE 1

Results for the Titration of Phosphates with 0.161 N Mercuric Nitrate

| $PO_4^{3-}$ taken, mg/liter | $PO_4^{3-}$ found, mg/liter | Error, % |
|---|---|---|
| 28.40 | 28.42 | + 0.07 |
| 22.14 | 22.27 | + 0.58 |
| 11.01 | 10.84 | − 1.53 |
| 5.17 | 5.06 | − 2.12 |
| 4.03 | 3.45 | −14.39 |
| 2.61 | 2.08 | −20.31 |

In order to study the accuracy of the method we had developed, $PO_4^{3-}$ ions at various concentrations were potentiometrically titrated with 0.161 N mercuric nitrate.

It is evident from Table 1 that the error increases with decreasing phosphate concentration. For concentrations not less than 5 mg/liter, the accuracy of the potentiometric titration was satisfactory. The reproducibility of the results for potentiometric titration of phosphates was good.

Addition of alcohol to the solution being titrated made it possible to lower the titration error for small amounts of $PO_4^{3-}$ ions, since alcohol, on the one hand, being a surface-active agent, lowers adsorption, while on the other hand, it lowers the solubility of the precipitates [3, 4].

The soil extracts tested often contain colloidal materials; nevertheless, the latter did not interfere with the titration of phosphate ions. Addition of gelatine to the test solution in amounts which were 20-100 times the $PO_4^{3-}$ ions present, had almost no effect on the results. Larger amounts of gelatin (up to 600 mg) gave solutions which were so viscous that titration became difficult.

As noted above, during titration of small amounts of phosphate ions, there was observed a significant shift of the break on the titration curve from the equivalence point. Titration errors could be lowered considerably, and, sometimes even reduced to zero, by carrying out the determination of the phosphate ions by

the double addition method. This technique of Shakhkel'dian has been used on several occasions [5-8].

It is clear from Table 2, that during the determination of small amounts of phosphate ions without using the double addition method the experimental error varies from 15.8 to 23.9%, while when this method is adopted

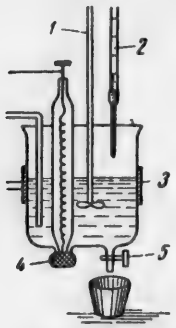



Fig. 1. Mercury indicator electrode: 1) Stirrer; 2) buret containing titrant; 3) titration beaker; 4) mercury indicator electrode; 5) tap for pouring off liquid which has been titrated.

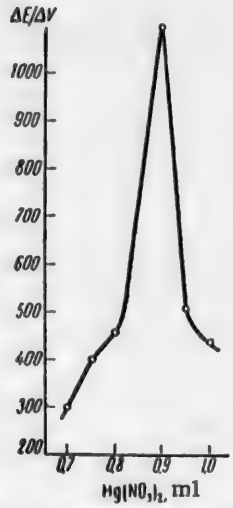



Fig. 2. Potentiometric titration curve for 5.47 mg $PO_4^{3-}$ ions with 0.188 N $Hg(NO_3)_2$.

the error varies from 0 to 4.7%. Thus, the double addition method is a better method from the point of simplicity and rapidity than the method of applying corrections for titration errors. Many test materials (minerals, soils, natural water) contain, as a rule, large amounts of chloride ions. On addition, however, of chlorides to

TABLE 2

Potentiometric Titration of Phosphate Ions using the Double Addition Method

| $PO_4^{3-}$ taken, mg | $PO_4^{3-}$ found, mg | Error % | $PO_4^{3-}$ taken, mg | First addition of $PO_4^{3-}$, mg | $Hg(NO_3)_2$ used for titration, ml | Second addition of $PO_4^{3-}$, mg | $Hg(NO_3)_2$ used for titration, ml | $PO_4^{3-}$ found, mg | Error, % |
|---|---|---|---|---|---|---|---|---|---|
| 4,10 | 3,45 | 15,8 | 4,10 | 1,37 | 0,9 | 23,35 | 4,6 | 4,00 | 2,4 |
| 4,10 | 3,45 | 15,8 | 4,10 | 1,37 | 0,9 | 6,84 | 1,8 | 4,10 | 0 |
| 4,10 | 3,45 | 15,8 | 4,10 | 1,37 | 0,9 | 17,78 | 3,7 | 3,91 | 4,5 |
| 2,73 | 2,08 | 23,9 | 2,73 | 2,73 | 0,9 | 19,35 | 3,7 | 2,65 | 2,9 |
| 2,73 | 2,08 | 23,9 | 2,73 | 2,73 | 0,9 | 8,19 | 1,8 | 2,73 | 0 |
| 2,73 | 2,08 | 23,9 | 2,73 | 2,73 | 0,9 | 24,62 | 4,6 | 2,60 | 4,7 |

the test solution in amounts which were 10-100 times that of the $PO_4^{3-}$ ions, the titration results for the phosphate ions did not change; thus chlorides do not interfere with the quantitative determination of $PO_4^{3-}$. It is possible to carry out successive titration of phosphate and chloride ions. In Fig. 3, is shown the titration curve obtained for a solution containing both chloride and phosphate ions. $PO_4^{3-}$ ions are titrated first and then the chloride ions.

Titration of solutions containing phosphates can be carried out within a wide pH range of 10 to 3. At pH < 3 in the original solution, the accuracy of the potentiometric titration method decreases because of the increase in solubility of the precipitate of $Hg_3(PO_4)_2$ formed during titration.

Under the conditions we used, $Ca^{2+}$, $Ba^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$ do not interfere.

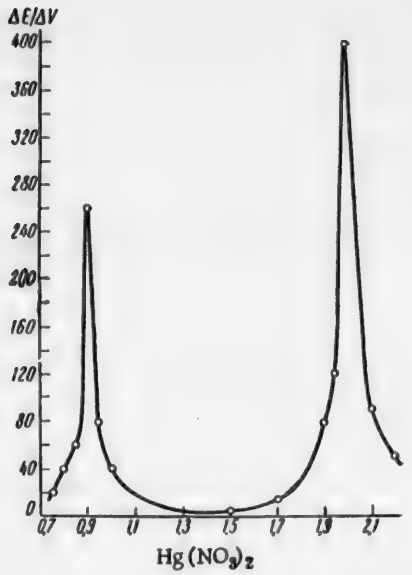



Fig. 3. Potentiometric titration curves for 5.47 mg $PO_4^{3-}$ ions in the presence of 7.16 mg Cl, using 0.188 N $Hg(NO_3)_2$ as titrant.

The method which we had developed for determination of phosphates was checked on samples of minerals (Table 3).

1 g of the mineral was introduced into a conical flask and dissolved in 30 ml of aqua regia by heating and constant agitation of the contents of the flask over a period of 30 minutes. The hot solution was neutralized with 2 N NaOH to a weak alkali reaction; it was then filtered into a 200 ml standard flask; the filtrate was cooled and its volume made up to the mark with distilled water. An aliquot (50 ml) of this solution was transferred to the titration beaker, and titrated with mercuric nitrate solution. When the phosphate content was low the double addition method was used.

The equivalence point during titration was found on addition of 8.10 ml of $Hg(NO_3)_2$ solution. The total $PO_4^{3-}$ content of the sample of mineral was 19.28%.

When the gravimetric method based on precipitation in the form of pyrophosphate (double precipitation) was used, the value found was 19.46%. Accordingly, the potentiometric titration method is as accurate as the gravimetric method, and has the advantages that it is quicker and simpler (an analysis takes 1.5-2 hours).

TABLE 3

Potentiometric Titration of Phosphate Ions in a Mineral Brought Back by the Geological Expedition of the Rostov State University to the Kamenskii Region; the Mineral was Found on the Right Bank of the River Don near Beshenskii ($T_{Hg(NO_3)_2/PO_4^{3-}}$ = 0.00595 g)

| $Hg(NO_3)_2$ solution used, mg | emf established, millivolts | ΔE | ΔV | $\frac{\Delta E}{\Delta V}$ | $Hg(NO_3)_2$ solution used, mg | emf established, millivolts | ΔE | ΔV | $\frac{\Delta E}{\Delta V}$ |
|---|---|---|---|---|---|---|---|---|---|
| 7,50 | 476 | — | — | — | 8,00 | 502 | 7 | 0,05 | 140 |
| 7,60 | 477 | 1 | 0,10 | 10 | 5,05 | 512 | 10 | 0,05 | 200 |
| 7,70 | 479 | 2 | 0,10 | 20 | 8,10 | 530 | 18 | 0,05 | 360 |
| 7,80 | 482 | 3 | 0,10 | 30 | 8,15 | 540 | 10 | 0,05 | 200 |
| 7,85 | 486 | 4 | 0,05 | 80 | 8,20 | 545 | 5 | 0,05 | 100 |
| 7,90 | 490 | 4 | 0,05 | 80 | 8,30 | 548 | 3 | 0,10 | 30 |
| 7,95 | 495 | 5 | 0,05 | 100 | 8,40 | 551 | 3 | 0,10 | 30 |

## SUMMARY

1. A method involving the use of a mercury indicator electrode has been developed for the potentiometric titration of $PO_4^{3-}$ ions. It was found that with decreasing phosphate concentration the experimental error increased. However, addition of ethanol to the solution being titrated improves the experimental results; this improvement is the result of a decrease in the solubility of the precipitate of $Hg_3(PO_4)_2$.

The double addition method led to a significant decrease in the experimental error during the determination of low concentrations of phosphate ions.

2. The reproducibility of the method is good. Good results can be obtained at a pH of 3-4 and higher.

3. Colloidal materials do not affect the results of the determination of phosphate ions. Chloride ions do not interfere with determination of $PO_4^{3-}$ ions. Furthermore, it is possible to carry out successive titration of $PO_4^{3-}$ and $Cl^-$ ions. $Ca^{2+}$, $Ba^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$ ions do not interfere.

4. Satisfactory results were obtained during the analysis of minerals.

## LITERATURE CITED


[1] I. Kolthoff and L. Fourman, "Potentiometric Titration", [Translated from English] ONTI, Leningrad, 1935.

[2] P. M. Babenyshev, Candidate's Thesis, 1951.*

[3] P. K. Agasyan, Bull. Moscow University, Phys. Math. and Natural Sciences Section, No. 2, 67-75 (1949).

[4] P. K. Agasyan, Bull. Moscow University, Phys. Math. Section, No. 8, 121-125 (1953).

[5] A. B. Shakhkel'dian, J. Appl. Chem. 2, 134, 467 (1929).

[6] A. B. Shakhkel'dian, J. Appl. Chem. 10, 1303 (1937).

[7] A. B. Shakhkel'dian, Sci. Trans. Saratov University 4, 5 (1940).

[8] A. B. Shakhkel'dian, J. Appl. Chem. 11, 692 (1938).



Received September 23, 1957


*In Russian.

# DETERMINATION OF ELEMENTAL SULFUR BY EXTRACTION WITH CARBON TETRACHLORIDE

V. P. Gladyshev

Kazakh State University, Alma-Ata

Current methods for the determination of elemental sulfur are fairly time consuming and difficult. The methods most frequently used are extraction of sulfur with carbon disulfide and the sulfite method [1]. In the method where extraction with carbon disulfide is used, the sulfur is weighed after distilling off the carbon disulfide, or the sulfur is oxidized to sulfate which is then precipitated as barium sulfate. This method has a number of technical drawbacks: extraction is carried out in diffused light to prevent decomposition of the carbon disulfide, while the volatility and the high inflammability of this solvent demand great care. Determination of elemental sulfur by this method takes 5-6 hours [1]. When elemental selenium, which is readily soluble in carbon disulfide, is present, it must be removed prior to determination of the sulfur.

The simplest method, from the practical point of view, is the sulfite method which is based on extraction of sulfur with an aqueous solution of sodium sulfite: $Na_2SO_3 + S = Na_2S_2O_3$; the thiosulfate formed is titrated with iodine solution. The sulfite method is inapplicable in the presence of polysulfides, since the latter, like elemental sulfur, interact with sulfite [2]. This method also cannot be used when elemental selenium is present, since selenium dissolves in the sulfite: $Na_2SO_3 + Se = Na_2SO_3Se$.

Water-soluble compounds of arsenic, iron, copper, etc., which react with iodine, also introduce considerable complications into the method for the determination of sulfur.

The cyanide method of Castiloni [3] is less widely used; this method is based on the interaction of elemental sulfur with potassium cyanide in an acetone medium with formation of a thiocyanate: KCN + S = KSCN (when tellurium is present, a tellurocyanate is formed). After removal of acetone by distillation the residue is dissolved in water and the thiocyanate determined argentometrically. Romm [3] used this method for the determination of elemental sulfur in slime from salt lakes, but substituted the argentometric finish by a photometric finish with ferric salts. The method gives good results, the use of potassium cyanide is, however, connected with some disadvantages.

A rapid method based on distilling off the elemental sulfur has been developed by Libina, Miller, and Musakin [2]. The experimental technique involved is simple and permits determination of elemental sulfur in materials containing sulfates, thiosulfates, and polysulfides in the course of 15-20 minutes. This method is inapplicable when the test material contains readily distilled compounds of mercury, and arsenic.

Details of a polarographic method for determining elemental sulfur have also been published [4], however, this method has only been worked out for the analysis of petroleum (elemental sulfur content of $10^{-2}$ – – $10^{-4}$%). The polarographic method is not applicable when the elemental sulfur content is high.

Materials which we have had to analyze contained large amounts of the sulfides of mercury and other metals, arsenic and antimony oxides, and various sulfur-containing compounds: thiosulfates, sulfates, sulfites, and polythionates. The elemental-sulfur content of these materials varied from 2-10%. Our problem was therefore to develop a convenient method for the determination of elemental sulfur in such materials. The most suitable technique for this purpose is extraction of elemental sulfur with some organic solvent. In addition to carbon disulfide, elemental sulfur also dissolves in benzene, toluene, chloroform, and carbon tetrachloride. The solubility of elemental sulfur in carbon tetrachloride is about 2% at 50° [5].

Carbon tetrachloride has a number of advantages over carbon disulfide as an extractant for sulfur. The considerably higher boiling point of carbon tetrachloride (76°) as compared with that of carbon disulfide permits extraction to be carried out more rapidly. There is no need to observe the precautions which are necessary on account of the inflammability of carbon disulfide. For the determination of large amounts of sulfur extraction can be carried out directly in a conical flask fitted with an air condenser.

Results for the determination of elemental sulfur in synthetic mixtures and in rocks, by the sulfite method and by extraction with carbon tetrachloride are given in Tables 1 and 2.

TABLE 1

Determination of Elemental Sulfur in Synthetic Mixtures Made up from Finely Ground Silicate Rock and Elemental Sulfur

| Sample wt., g | Elemental sulfur content, % | | | | |
|---|---|---|---|---|---|
| | taken | found | | | |
| | | by the sulfite method [1] | | by extraction with $CCl_4$ | |
| 5,0 | 0,10 | 0,10 | 0,11 | 0,10 | 0,10 |
| 5,0 | 0,10 | 0,10 | 0,09 | 0,10 | 0,10 |
| 5,0 | 0,25 | 0,25 | 0,24 | 0,24 | 0,26 |
| 5,0 | 0,50 | 0,48 | 0,49 | 0,48 | 0,49 |
| 2,0 | 0,75 | 0,73 | 0,74 | 0,72 | 0,73 |
| 2,0 | 1,00 | 1,03 | 1,02 | 1,02 | 1,02 |
| 2,0 | 1,00 | 1,01 | 1,00 | 0,98 | 1,02 |
| 1,0 | 2,50 | 2,48 | 2,52 | 2,50 | 2,56 |
| 1,0 | 5,00 | 5,07 | 5,04 | 5,09 | 4,98 |
| 1,0 | 5,00 | 5,07 | 5,09 | 5,08 | 5,07 |

TABLE 2

Determination of Elemental Sulfur in Rocks

| Sulfur found, % | | | | | Relative error, % |
|---|---|---|---|---|---|
| by the sulfite method | by extraction with $CCl_4$ | | | | |
| | | | | Mean | |
| 0,74 | 0,70 | 0,76 | 0,75 | 0,74 | — |
| 1,42 | 1,40 | 1,46 | 1,48 | 1,44 | +1,4 |
| 0,49 | 0,54 | 0,52 | 0,52 | 0,53 | +8,2 |
| 2,33 | 2,25 | 2,36 | 2,30 | 2,27 | —2,4 |
| 0,90 | 0,85 | 0,87 | 0,84 | 0,85 | —5,5 |

Having obtained consistent results for the determination of elemental sulfur in synthetic mixtures and rocks, we determined sulfur in materials containing oxides, sulfates, sulfites, and other salts of sulfur-containing acids.

Analytical results were controlled by carrying out the determinations on samples of varying weights. The results obtained are given in Table 3.

TABLE 3

Determination of Elemental Sulfur in Materials Containing Oxides, Sulfides, Sulfates, and Other Compounds

| Elemental sulfur found, % | | | | | Mean content, % |
|---|---|---|---|---|---|
| sample weight, g | | | | | |
| 0,5 | 1,0 | 1,0 | 2,0 | 2,0 | |
| 1,80 | 1,79 | 1,74 | 1,82 | 1,80 | 1,79 |
| 2,71 | 2,69 | 2,68 | 2,72 | 2,70 | 2,70 |
| 6,02 | 5,98 | 5,96 | 6,14 | 6,07 | 6,03 |
| 10,24 | 10,30 | 10,21 | 10,37 | 10,12 | 10,24 |

These results show that it is possible to determine elemental sulfur by the suggested method in complex materials.

The presence of small amounts of elemental selenium and tellurium (up to 0.5%) in the test materials does not affect the experimental results for sulfur.

Experimental procedure for the determination of elemental sulfur. For sulfur contents not greater than 0.1%, 0.5-2 g of test material is taken for determination of elemental sulfur, while for lower sulfur contents, 2-5 g

of test material is taken. The sample is prepared for analysis in the same way as that described for extraction with carbon disulfide [1]. For sulfur contents less than 0.1%, the sulfur is extracted with carbon tetrachloride in a Soxhlet apparatus for 1-1.5 hours. After extraction is complete, the flask with the extracted sulfur is disconnected from the Soxhlet apparatus and the carbon tetrachloride distilled off by heating the flask on a naked flame (the carbon tetrachloride is distilled off under a forced draught). When only 2-3 ml of carbon tetrachloride is left in the flask, the rest is evaporated off on a sand bath heated to 75-80° and covered with an asbestos board. The crystalline sulfur formed after evaporationg the carbon tetrachloride is then weighed.

For elemental sulfur contents greater than 0.1-0.2% the procedure can be simplified considerably (in such cases extraction can be carried out in a conical flask fitted with an air condenser rather than in a Soxhlet).

An aliquot is placed in a 100 ml conical flask and 50 ml of carbon tetrachloride added; the flask is fitted with an air condenser and the whole heated at 50-60° on a sand bath covered with an asbestos sheet, or on an asbestos grid for 1 hour. At the end of this time the reflux condenser is disconnected and the solution obtained filtered into another 100 ml flask through a fine paper filter by decantation. In order to prevent sulfur crystallizing out during filtration, funnel and flask should be heated beforehand to 45-50°. The residue from which the solution has been decanted is extracted again, by adding 10 ml of carbon tetrachloride and heating for 5-10 minutes at 50-60°. This solution in turn is poured onto the filter. The filter is washed with two lots of 3-5 ml of carbon tetrachloride heated to 50°. All the solutions are combined. The carbon tetrachloride is then evaporated off (under a forced draught) as indicated above. The sulfur is finally weighed.

When bitumen or some other organic material is present, the elemental sulfur is determined by the sulfite method after distilling off the solvent.

## SUMMARY

A simple method has been developed for the determination of elemental sulfur by extraction with carbon tetrachloride; the method is applicable to the determination of sulfur in materials which are difficult to analyze by the methods suggested earlier. The method has been tested on rocks and other materials containing from 0.5 to 10% of elemental sulfur.

## LITERATURE CITED

[1] "Analysis of Mineral Raw Materials", Edited by Yu. N. Knipovich and Yu.V. Morachevskii [in Russian] Second Edition, Goskhimizdat, Leningrad, 1956.

[2] R. I. Libina, A. D. Miller, and A. N. Musakin, Industrial Labs. 16, 259 (1950).

[3] I. L. Romm, J. Appl. Chem. 17, 188 (1944).

[4] R. D. Obolentsev, B. V. Aivazov, and A. A. Ratovskaya, J. Anal. Chem. 12, 134 (1957).*

[5] J. H. Hildebrand and C. A. Jenks, J. Amer. Chem. Soc. 43, 2172 (1921).

Received January 30, 1958

*Original Russian pagination. See C.B. Translation.

# CHEMICOSPECTROGRAPHIC ANALYSIS OF METALLIC BERYLLIUM AND BERYLLIUM OXIDE OF HIGH PURITY

A. G. Karabash, Sh. I. Peizulaev, R. L. Slyusareva, and V. M. Lipatova

Several monographs have been devoted to the chemistry and analytical chemistry of beryllium [1-3]. Chemical methods for the analysis of metallic beryllium and its compounds for the amount of impurities contained in them have been described in a number of papers [4-8]. A bibliography devoted to this question has been given in a special review [8]. Most of the chemical techniques specify determination of the elements in separate aliquots. In one textbook [4] methods are given for the determination of impurities in pure beryllium; of these impurities Fe, Al, Si, and BeO are determined photometrically. Methods have also been published for the direct spectrographic determination of impurities in beryllium [9-10]. The evaporation method has been adopted for the spectrographic determination of boron present as an impurity in beryllium, and the possibility has been demonstrated of determining some other impuritiesby this method [11].

The chemicospectrographic method of analysis described below is designed for controlling high purity beryllium and beryllium oxide

The chemicospectrographic method permits simultaneous determination of the following 24 elements present as impurities: Mg, Ca, Ba, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Pb, Sb, Bi, Ga, In, Tl, Te. Sodium is determined separately on a glass spectrograph.

Concentration of impurities is effected by removal of beryllium by extraction in the form of its basic acetate $Be_4O(CH_3COO)_6$ with chloroform. Basic beryllium acetate has some very characteristic properties [1,2]. It is fairly stable to the action of many inorganic reagents (water, hydrochloric acid) and readily dissolves in acetic acid, chloroform, nitrobenzene, benzene, toluene, benzine, kerosene, acetone, carbon disulfide, carbon tetrachloride, etc. The characteristic properties of beryllium acetate, coupled with its covalent structure [12] are responsible for the high selectivity of its extraction separation. The solubility of basic beryllium acetate in chloroform is 50 g per 100 ml of $CHCl_3$, while the acetates of the metals being determined in beryllium are almost insoluble. There are published references to the use of basic beryllium acetate for separating beryllium and aluminum, beryllium and iron [13-14], and also for the preparation of pure standard solutions of beryllium and pure beryllium oxide; the techniques used in these instances were extraction of the basic acetate by organic solvents (carbon tetrachloride, toluene, or xylene) [15] and also sublimation [16-18].

In the work described here a study was made of the behavior of the 24 elements mentioned above, during extraction of basic beryllium acetate with chloroform.

For extracting the impurities, basic beryllium acetate was dissolved in chloroform, and the chloroform solution washed three times with hydrochloric acid (4 N) in a separating funnel. During this operation the impurities were quantitatively transferred into the hydrochloric wash liquor together with a small amount of beryllium (about 1/20 of the original sample taken).

Completeness of the extraction of the impurities into the concentrate during chloroform extraction of basic beryllium acetate was tested in experiments with synthetic mixtures of salts. Impurity elements in amounts ranging from $10^{-3}$ – $10^{-5}$% with respect to beryllium were added to spectrographically pure beryllium acetate. The mixture was treated and extraction carried out under the conditions used in the method developed. Each phase was analyzed – the hydrochloric wash liquor and the chloroform extract – by the most sensitive

chemical and spectrographic methods. On the basis of a large number of experiments, mean values of the percentage extraction of traces of the elements into the concentrate (from 85-100%) were found. These values were confirmed in experiments with synthetic mixtures, and also during the analysis of metallic beryllium and beryllium oxide — by checking on the purity of the basic acetate after the chloroform extraction.

In the case of Cd, Cu, Co, Sb, Ag, Fe, Ca, Mn, Cr, Mo, Sn, Zn, In, Na, completeness of extraction was also checked by means of radioactive indicators.

From the hydrochloric acid wash liquor into which part of the beryllium had passed (about 1/10 of the original aliquot) as well as all the impurities, a powdered concentrate of the impurities was prepared. The basis of this concentrate was beryllium oxide in the glass-like form. The latter was prepared as follows: a solution of beryllium nitrate was evaporated to a sirupy state when beryllium hydroxide was precipitated by addition of excess 25% ammonia solution. The thick paste of beryllium hydroxide was dried and calcined until the ammonium nitrate had been completely decomposed. Decomposition of $NH_4NO_3$ (at 200°) is preceded

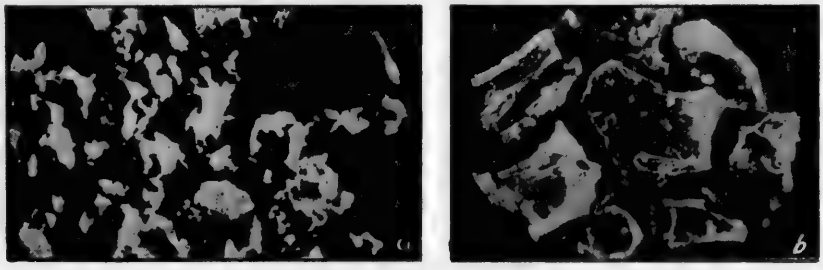


Fig. 1. Microphotographs of beryllium oxide: a) Beryllium oxide prepared from the nitrate by calcining at 1000° (dust-form); b) glass-like oxide prepared by the method developed, and used as a basis for spectrographic analysis.

by its fusion which starts at 165°, so that formation of beryllium oxide takes place under these conditions in the presence of molten ammonium nitrate. The oxide prepared in this way is a dense, granular powder having the appearance of large transparent glass-like grains with a strong luster; it differs sharply from the usual dust-like beryllium oxide (Fig. 1). X-ray structural studies* of the glass-like beryllium oxide showed that it has a hexagonal crystalline lattice of the Wurtzite type which is characteristic of the usual type of BeO, but it differs from the latter in having appreciably smaller crystal dimensions which approximate to those of colloidal particles; this determines its glass-like character. The bulk density of the glass-like oxide is considerably greater than that of the usual, dust-like BeO (twice that of the usual oxide calcined at 1000° and 5 times that of the ordinary partially hydrated oxide). This means that it is possible to pack more of the oxide in the electrode, and this accordingly increases the sensitivity of the spectrographic determinations. The glass-like oxide powder does not raise dust when it is scattered, and it is readily loaded into the crater in the carbon electrode.

An unenriched sample was prepared at the same time as the chemical concentrate of impurities. Preparation of the unenriched sample consisted of converting it into beryllium oxide in the glass-like form, this being identical with the final stage of the preparation of the concentrate of the impurities. The spectra of the concentrate of the impurities and of the unenriched sample were then photographed together; this enabled the range of concentrations determined to be extended, and to cover the concentration range $1 \times 10^{-1}$ to $1 \times 10^{-5}$%.

The standards for spectrographic analysis were prepared by adding known amounts of standard solutions of the impurity elements to a solution of spectrographically pure beryllium nitrate, and then preparing the glass-like beryllium oxide from the resultant solution.

For controlling the purity of less pure samples, where there is no need for chemical concentration, it is possible to carry out a direct spectrographical analysis of the unenriched samples using the same standards.

*X-ray structural investigations were carried out by E. S. Makarov.

The sensitivity of the determination of impurities when preliminary concentration is not used is $10^{-3}$ – $10^{-4}$%, while when concentration is used the sensitivity is $10^{-4}$ – $10^{-5}$% (Table 1).

a. Preparation of the chemical concentrate of impurities. 2 g of beryllium (or 5.6 g of beryllium oxide) is dissolved in 90 ml of 6 N HCl plus 10 ml of 14 N $HNO_3$ contained in a quartz beaker, and the solution evaporated to a sirupy consistency. By a three-stage evaporation with nitric acid (50 ml the first time and 20 ml each the second and third times) to dryness, beryllium nitrate is obtained. Concentrated ammonia is then added to precipitate beryllium hydroxide in the form of a paste; the latter is dried and then calcined, the temperature being brought up slowly to 250-300°. The oxide obtained is dissolved in 100 ml glacial acetic acid, and, after evaporating the solution to dryness, basic beryllium acetate is obtained.

When beryllium oxide which has been calcined at a temperature not higher than 600° is to be analyzed, it can be dissolved directly in glacial acetic acid; after evaporation of the solution thus obtained basic beryllium acetate is prepared.

The basic beryllium acetate is dissolved in 100 ml chloroform. The chloroform solution is washed three times in a separating funnel with 4 N hydrochloric acid; the first time with 30-40 ml of the acid, the second and third times with 20 ml. The hydrochloric acid wash liquors are evaporated in a quartz basin preliminarily heated to 500° and weighed. The sirupy solution is treated three times with nitric acid (first 8 ml and then two lots of 3 ml), the mixture being evaporated each time to a sirupy state. Beryllium hydroxide is precipitated

TABLE 1

Analytical Lines and the Sensitivity of Determination of Impurity-Elements in Beryllium

| Element | Sensitivity (as a % of metallic Be) during analysis without enrichment | Sensitivity (as a % of metallic Be) during analysis of the conc. of impur. K-20 | Analytical line, A | Element | Sensitivity (as a % of metallic Be) during analysis without enrichment | Sensitivity (as a % of metallic Be) during analysis of the conc. of impur. K-20 | Analytical line, A |
|---|---|---|---|---|---|---|---|
| Mg* | $3\cdot10^{-4}$ | $1\cdot10^{-4}$ | 2802,7 | Ag | $3\cdot10^{-4}$ | $2\cdot10^{-5}$ | 3280,7 |
| Ca* | $2\cdot10^{-3}$ | $3\cdot10^{-4}$ | 4226,7 | Zn | $1\cdot10^{-2}$ | $5\cdot10^{-4}$ | 3345,0 |
| Ba | $3\cdot10^{-3}$ | $2\cdot10^{-4}$ | 4934,1;2335,3 | Cd | $1\cdot10^{-4}$ | $5\cdot10^{-6}$ | 2288,0 |
| Al* | $2\cdot10^{-3}$ | $3\cdot10^{-4}$ | 3082,2 | Sn | $2\cdot10^{-3}$ | $1\cdot10^{-4}$ | 2840,0 |
| Ti | $3\cdot10^{-3}$ | $2\cdot10^{-4}$ | 3349,0 | Pb | $2\cdot10^{-3}$ | $1\cdot10^{-4}$ | 2833,1 |
| V | $1\cdot10^{-3}$ | $5\cdot10^{-5}$ | 3184,0;2688,0 | Sb | $3\cdot10^{-3}$ | $2\cdot10^{-4}$ | 2598,1 |
| Cr | $1\cdot10^{-3}$ | $5\cdot10^{-5}$ | 2835,6 | Bi | $1\cdot10^{-3}$ | $5\cdot10^{-5}$ | 3067,7 |
| Mo | $2\cdot10^{-3}$ | $1\cdot10^{-4}$ | 2816,2 | Te | $3\cdot10^{-3}$ | $2\cdot10^{-4}$ | 2385,8 |
| Mn | $2\cdot10^{-4}$ | $1\cdot10^{-5}$ | 2576,1 | Ga | $1\cdot10^{-3}$ | $5\cdot10^{-5}$ | 2874,2 |
| Fe* | $1\cdot10^{-3}$ | $2\cdot10^{-4}$ | 2599,4 | In | $3\cdot10^{-3}$ | $2\cdot10^{-4}$ | 3256,1 |
| Co | $2\cdot10^{-3}$ | $1\cdot10^{-4}$ | 3412,6 | Tl | $3\cdot10^{-3}$ | $2\cdot10^{-4}$ | 2767,9 |
| Ni | $2\cdot10^{-3}$ | $1\cdot10^{-4}$ | 3050,8 | Na* | $2\cdot10^{-3}$ | $1\cdot10^{-4}$ | 5890,0 |
| Cu* | $2\cdot10^{-4}$ | $3\cdot10^{-5}$ | 3247,5 | | | | |

*The sensitivity indicated for the determination of Na, Mg, Ca, Al, Fe, and Cu takes into account their possible content in the control experiment.

with concentrated ammonia, and the paste of hydroxide thus formed, dried and calcined, the temperature being gradually taken up to 300°. After removal of the ammonium nitrate the mass is calcined for a further half-hour at 500°. The residue is weighed and the enrichment coefficient of the impurity in the concentrate is calcined; this coefficient is equal to the ratio of the original aliquot (in terms of BeO) to the amount of concentrate obtained. Usually, the weight of the concentrate is about 100 mg – in terms of the metal – i.e., the enrichment coefficient is 20-25.

At the same time a blank is carried out in which all the reagents are used. The blank is carried out by adding to the hydrochloric acid solution obtained during the extraction, a solution of spectrographically pure beryllium nitrate in an amount corresponding to 100 mg of Be, this serves as the basis for spectrographical analysis.

b. Preparation of the unenriched sample. 0.2 g of metal (or 0.56 g of the oxide) is dissolved in 10 ml of 6 N HCl plus 1 ml of 14 N $HNO_3$ contained in a quartz basin. The solution obtained is evaporated to a sirupy state, and by treatment with three lots of nitric acid (8 ml, 3 ml, 3 ml) beryllium nitrate is obtained. When beryllium oxide which has not been heated below 1000° is to be analyzed, it can be dissolved directly in nitric acid. Beryllium hydroxide is precipitated as a paste by addition of concentrated ammonia, the hydroxides are then dried and finally calcined, the temperature being gradually taken up to 300°; it is finally heated for half an hour at 500°. The glass-like beryllium oxide is ground up in a quartz mortar and pestle and is then ready for spectrographic analysis.

In order to carry out a blank, spectrographically pure beryllium oxide (or beryllium nitrate) is subjected to the same operations, the same reagents being used as for the sample.

The water, hydrochloric, nitric, and acetic acids used for the work are purified by distillation in quartz apparatus and stored in quartz flasks. Ammonia solution (about 25%) is prepared by saturating twice-distilled water with ammonia by diffusion. For this purpose, the distilled water contained in a quartz flask is placed in a desiccator, in which is also placed a concentrated solution of reagent ammonia to which lumps of NaOH have been added. Quartz beakers, basins and rods are used.

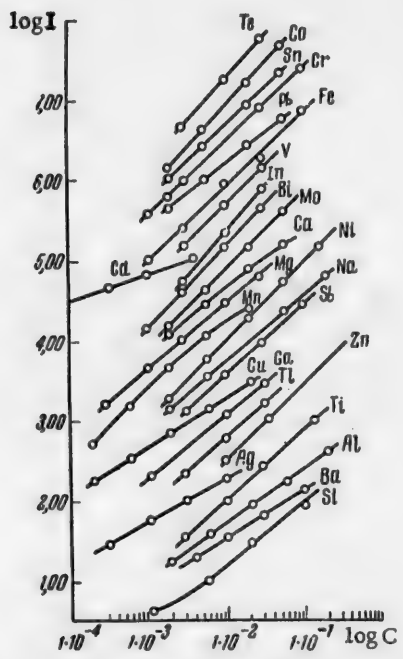



Fig. 2. Calibration curves for the determination of impurities in beryllium. The curves are shifted arbitrarily along the ordinate to avoid intersection.

c. Spectrographic determination of impurities. The spectra of the concentrate of the impurities, sample without enrichment, control tests, and standards are all photographed on the same photographic plate. 24 impurity elements can be determined from one spectrogram. Sodium is determined independently in a separate series of standards on a glass spectrograph. The carbon electrodes are fired in a dc arc at a current strength of 12 amps. for 15 seconds in order to purify them from accidental contamination. The lower electrode is a carbon rod with a crater 4 mm in diameter and 6 mm deep, while the upper electrode is a rod sharpened to a cone. The weight of powder loaded into the electrode is 50 mg. In order to fix the powder in the electrode crater, the powder is moistened with 3 drops of a 20% alcoholic solution of bakelite and the electrode then dried on an electric hot plate for 10-15 minutes. This precaution is essential in order to prevent the friable beryllium oxide powder from being thrown out of the crater during the initial stages of arc burning. The spectra are excited in a dc arc at a current strength of 12 amps, they are photographed in a ISP-22 spectrograph at a slit width of 10 $\mu$. A two-stage attenuator with a relative transmission of 1 : 10 is fitted in front of the slit. Exposure time is 2 minutes; during this time complete combustion of the sample takes place. The photographic plates used are spectrographic type II.

The conditions used for determination of sodium are as follows: spectrograph ISP-51, slit width 10 $\mu$, ac arc, current 5 amps, photographic plates panchrome. The lower electrode is a carbon rod with a crater 4 mm in diameter and 4 mm deep, while the upper electrode is a carbon rod sharpened to a cone. The subsequent procedure adopted for treatment of the results is the same as for determination of the remaining impurities.

Impurity lines and background are photometrically measured. In the short-wave part of the spectrum, the lines are measured photometrically in the strong stage of the spectrogram, while in the long wave part of the spectrum the lines are measured in the weak stage of the spectrogram. Calibration curves (Fig. 2) are

constructed within the coordinates (log I, log C).* Conversion from blackening to intensity is carried out in a special calculating machine. For determination of the impurities in the concentrate, the result obtained by means of the calibration curve is divided by the enrichment coefficient; in this way the content of a given impurity in the original sample is obtained.

The analytical lines used and the sensitivity of the determination of the impurities are given in Table 1.

The accuracy and reproducibility of the method was checked by analyzing synthetic mixtures (25 mixtures, to each of which was added 20-25 elements), and also by comparing the results obtained during analysis of samples by the given method and by chemical methods (34 samples). The relative error, calculated as the mean arithmetic error of all of these determinations amounts to ±20%. Nevertheless, near the sensitivity limit, particularly in the presence of a strong background, individual errors may be as high as 50-100%. This is particularly true for the determination of cadmium; this is a consequence of two factors: the low value of the slope for its calibration curve (Fig. 2), and the low contrast in the 2280 A region.

TABLE 2

Results of the Analysis of Synthetic Mixtures (Containing Impurities Whose Contents are Given in Terms of Beryllium Metal)

| Element | Mixture 1, concentrate | | Mixture 2, without enrichment | |
|---|---|---|---|---|
| | added | found | added | found |
| Mg | $5{,}3\cdot10^{-4}$ | $5{,}5\cdot10^{-4}$ | $1{,}5\cdot10^{-2}$ | $1{,}4\cdot10^{-2}$ |
| Ca | $2{,}3\cdot10^{-3}$ | $2{,}6\cdot10^{-3}$ | $4{,}5\cdot10^{-2}$ | $6\cdot10^{-2}$ |
| Ba | $6\cdot10^{-4}$ | $5\cdot10^{-4}$ | $9\cdot10^{-3}$ | $1{,}1\cdot10^{-2}$ |
| Al | $1{,}4\cdot10^{-3}$ | $2{,}1\cdot10^{-3}$ | $1{,}5\cdot10^{-2}$ | $1{,}7\cdot10^{-2}$ |
| Ti | $6\cdot10^{-4}$ | $8{,}3\cdot10^{-4}$ | $9\cdot10^{-2}$ | $9{,}5\cdot10^{-2}$ |
| V | $2\cdot10^{-4}$ | $2{,}3\cdot10^{-4}$ | $6\cdot10^{-2}$ | $7{,}4\cdot10^{-2}$ |
| Cr | $2\cdot10^{-4}$ | $2\cdot10^{-4}$ | $1{,}5\cdot10^{-2}$ | $1{,}4\cdot10^{-2}$ |
| Mo | $4\cdot10^{-4}$ | $4\cdot10^{-4}$ | $6\cdot10^{-2}$ | $5{,}6\cdot10^{-2}$ |
| Mn | $6{,}7\cdot10^{-5}$ | $8{,}7\cdot10^{-5}$ | $1{,}5\cdot10^{-2}$ | $1{,}3\cdot10^{-2}$ |
| Fe | $2{,}2\cdot10^{-3}$ | $1{,}8\cdot10^{-3}$ | $1{,}5\cdot10^{-2}$ | $1{,}7\cdot10^{-2}$ |
| Co | $4\cdot10^{-4}$ | $4{,}3\cdot10^{-4}$ | $3\cdot10^{-2}$ | $3\cdot10^{-2}$ |
| Ni | $4\cdot10^{-4}$ | $5\cdot10^{-4}$ | $4{,}5\cdot10^{-2}$ | $4{,}4\cdot10^{-2}$ |
| Cu | $9\cdot10^{-5}$ | $8\cdot10^{-5}$ | $1{,}5\cdot10^{-2}$ | $1{,}7\cdot10^{-2}$ |
| Ag | $6\cdot10^{-5}$ | $8\cdot10^{-5}$ | $1{,}5\cdot10^{-2}$ | $1{,}4\cdot10^{-2}$ |
| Zn | $2\cdot10^{-3}$ | $5\cdot10^{-3}$ | $9\cdot10^{-2}$ | $6{,}8\cdot10^{-2}$ |
| Cd | $2\cdot10^{-5}$ | $1\cdot10^{-5}$ | $9\cdot10^{-4}$ | $6\cdot10^{-4}$ |
| In | $2\cdot10^{-4}$ | $2{,}8\cdot10^{-4}$ | $2{,}6\cdot10^{-2}$ | $4{,}8\cdot10^{-2}$ |
| Sn | $4\cdot10^{-4}$ | $5\cdot10^{-4}$ | $6\cdot10^{-2}$ | $5{,}7\cdot10^{-2}$ |
| Pb | $4\cdot10^{-4}$ | $5{,}2\cdot10^{-4}$ | $4{,}5\cdot10^{-2}$ | $4\cdot10^{-2}$ |
| Sb | $6\cdot10^{-4}$ | $6{,}3\cdot10^{-4}$ | $4\cdot10^{-2}$ | $4{,}2\cdot10^{-2}$ |
| Bi | $2\cdot10^{-4}$ | $2\cdot10^{-4}$ | $2\cdot10^{-2}$ | $1{,}8\cdot10^{-2}$ |
| Ga | $2\cdot10^{-4}$ | $3\cdot10^{-4}$ | $6\cdot10^{-3}$ | $5{,}9\cdot10^{-3}$ |
| Tl | $2\cdot10^{-4}$ | $2{,}5\cdot10^{-4}$ | $2\cdot10^{-2}$ | $1{,}8\cdot10^{-2}$ |
| Te | $2\cdot10^{-4}$ | $1{,}9\cdot10^{-4}$ | $2\cdot10^{-2}$ | $1{,}9\cdot10^{-2}$ |

Table 2 contains, as examples, the results of analysis of synthetic mixtures with and without the use of concentration.

## SUMMARY

A chemicospectrographic method has been developed for the determination of 24 elements present as impurities in beryllium and its oxide. In order to concentrate the impurities (20-25 times) beryllium is separated in the form of its basic acetate by extraction with chloroform. The sensitivity of the determination of the ele-

*In those cases where the blackening of the line of the element being determined is located on the straight-line part of the characteristic curve of the photographic plate ($0.60 \leq \Delta S \leq 1.80$), the calibration curve is constructed with the coordinates ($\Delta S$, log C), where $\Delta S$ is the difference between the blackening of the line and the background.

ments is increased to $10^{-4} - 10^{-5}$%. The method can be used for the analytical control of the production of high-quality materials.

A method has been developed for the spectrographic analysis of samples without preliminary concentration of the impurities; this method, which can be used for controlling the production of commercial products, has a sensitivity of $10^{-3} - 10^{-4}$%.

## LITERATURE CITED


[1] Gmelins. Handbuch der anorganischen Chemie, S. N. 26, Beryllium, Berlin, 1930.

[2] N. V. Sidgwick, The Chemical Elements and their Compounds, V. I ,group 2A, Oxford, 1952, p. 195-218.

[3] R. Fresenius and G. Jander, Handbuch der analytischen Chemie, Teil III, Band 2a, Berlin, 1940, S. 76-90.

[4] H. Ginsberg, Leichtmetallanalyse, Berlin, 1955, S. 201-206.

[5] O. Proske and H. Blumenthal, Analyse der Metalle, Band I, Schiedsverfahren, 1949, S. 66-84.

[6] R. V. Mervel', J. Anal. Chem. 2, 103 (1947).

[7] R. W. Bane, Analyt. Chem. 27, N 6, 1022 (1955).

[8] F. A. Vinci, Analyt. Chem. 25, 1580 (1953).

[9] A. L. Smith and V. A. Fassel. Analyt. Chem. 21, 1095 (1949).

[10] P. M. Polyakov, A. K. Rusanov, and I. M. Blokh, Industrial Labs. 23, 1320 (1957).

[11] A. N. Zaidel', N. N. Kaliteevskii, L. V. Lipis, and M. P. Chaika, J. Anal. Chem. 12, 17 (1957).*

[12] M. L. Quinet, Comp. rend. 218, 757, 757 (1944).

[13] F. G. Haber and van Oordt, Z. Anorgan. Chem. 40, 466 (1904).

[14] H. Fischer, Wissenschaftliche Veroffentlichungen aus dem Siemens-Konzern, 5, N 2, 99-119 (1926).

[15] J. Besson and H. D. Hardt, Chem. Abstrs 46, 7927 (1952).

[16] H. C. Kawecki, Chem. Abstrs 47, 10184 (1953).

[17] H. C. Kawecki, Chem. Abstrs 47, 11678 (1953).

[18] Masayoshi Ishibashi and Kenji Motojima, Chem. Abstrs 46, 3449 (1952).


Received October 28, 1957

*Original Russian pagination. See C.B. Translation.

# A SEMI MICRO METHOD FOR THE ISOTOPIC ANALYSIS OF MATERIALS WITH A DEUTERIUM CONTENT APPROXIMATING TO 100%

A. I. Shatenshtein and Yu. I. Antonchik

The L. Ya. Karpov Physicochemical Institute

Modern physical methods of research make it possible to analyze compounds with high deuterium contents with reasonable accuracy (see [1], p. 5). Nevertheless, in those cases where these methods are for some reason difficult to carry out, the method described below, which does not require complicated apparatus can be used for isotopic analysis.

The test material (organic compound, ammonia) is burnt on cupric oxide under conditions which exclude ingress of atmospheric moisture, since the heavy water formed is very hygroscopic. The water formed, amounting to 0.2-0.3 ml is collected in a receiver containing calcium metal (for taking up the carbon dioxide and nitrogen oxides), and is distilled into a drawn-out test tube containing a quartz float which is used for measuring the density of the water.* Experimental accuracy is 0.05%.

## 1. Combustion of the Deuterium Compound

a. Combustion apparatus (Fig. 1). The material is burnt in tube 3 which is heated up to 700° by means of an electric oven. The reservoir 1 containing test material is sealed with an accurately fitting ground-glass cap. When ammonia is analyzed detail 10 is used instead of the cap, detail 10 is fitted by means of Wood alloy into a screw and is connected through a valve [2] with an ampoule containing the ammonia (Fig. 1, A). A receiver 5** is connected via a ground joint to the combustion tube. The system can be connected to the atmosphere or to a vacuum pump via an opening in joint 6. The apparatus ends up in tube 9 — in which the measurements are made — fitted with tap 7 connected to the receiver via a ground joint. 2, 4, and 8 are porous filters, filter 4 being fused in position after filling the tube with CuO. All the apparatus is made from quartz.

b. Preparation of the tube for combustion. Before each combustion, a stream of dry oxygen is passed through the heated tube for 20-30 minutes in order to oxidize any copper which has been formed by reduction during the previous combustion. The tube is then pumped out for a further 30-40 minutes in order to remove adsorbed moisture.

c. Combustion of organic material. A calibrated float is placed in tube 9, while a small lump (about 0.01 g) of pure calcium metal is placed in receiver 5. All joints and taps are smeared with vacuum grease and the apparatus is assembled. The test material is placed in reservoir 1. The ground joint of reservoir 1 is smeared with silicon grease and is then sealed with the cap. The system is connected to the vacuum pump via the opening in joint 6, and is exhaustively pumped out, using a vacustat for following the evacuation process. Taps 6 and 7 are closed and receiver 5 is cooled with liquid air, then by carefully heating reservoir 1 evaporation of the test material is commenced.

Whe evaporation is complete, the system is again evacuated for a short time. The Dewar vessel containing liquid air is removed, and the ice in the receiver allowed to melt; the water is then collected in the

*A micro float method has been developed by A. I. Shatenshtein and E. A. Yakovleva (see [1], p. 183).

** V. R. Kalinachenko's design [5].

of receiver 5. When this is done the oxides react with the calcium metal. Tap 7 is next opened, and by cooling tube 9 with liquid air the water is driven into it. Tap 7 is closed.

d. Combustion of ammonia. During the combustion of ammonia, nitrogen is formed which does not condense and gives rise to a pressure in the tube. Accordingly, combustion is not carried out in a vacuum. The system is assembled and pumped out so as to get rid of moisture as before, but then dry air is passed into the system through the opening in joint 6 which is connected to tubes packed with $P_2O_5$; on the side tube on joint 6 a bubble counter is fitted by means of a rubber tube; only after this has been done is the valve, to which

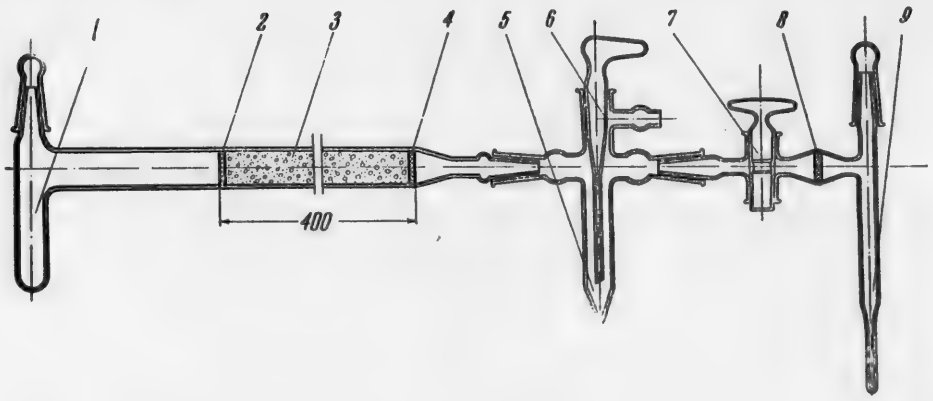



Fig. 1.

the ampoule containing the liquid ammonia (about 0.4 ml) is connected, opened and combustion commenced. When the stream of bubbles cease the system is evacuated; all subsequent operations are the same as those described above.

In order to ensure complete oxidation of ammonia it is necessary to carry out combustion slowly (2-2.5 hours).

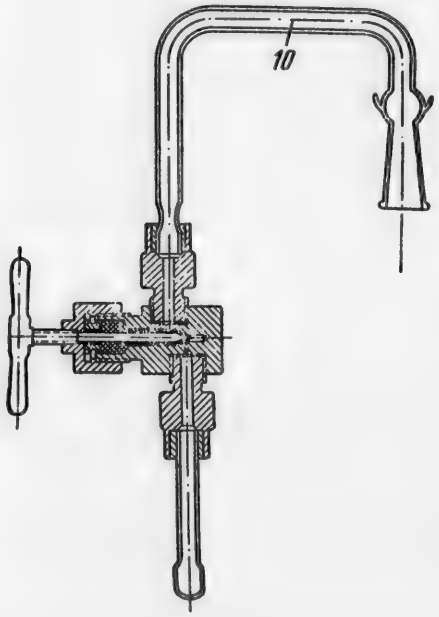



Fig. 2.

## 2. Isotopic Analysis of Water

The isotopic analysis of water reduces to the determination of the equilibrium flotation temperature of a micro-float, for which the equilibrium flotation temperature has been determined beforehand in heavy water with a known deuterium content similar to value to that expected for the test material. The deuterium concentration of the heavy water used for calibrating the float is established pycnometrically (see [1], p. 154).

A thermostat in which the temperature could be read and kept constant to an accuracy of $\pm$ 0.05° was used for the measurements. The temperature can be altered over a 10° range, which means that one float can be used for analyzing samples with deuterium concentrations differing within the limits of 2%.

In order to analyze preparations containing from 90 to 100% deuterium we used four floats calibrated by means of heavy water with deuterium concentrations ($C_1$) of 99.58, 97.89, 85.93, and 94.06%.

If the change in density of the quartz float (1.8 $\gamma$/ml per 1°) can be regarded as negligible, then the density of the water ($d_4^{t_1}$ st.) used for calibration at the

equilibrium flotation temperature of the float in it ($t_1$) can be assumed to be equal to the density of the test water ($d_{4\,test}^{t_2}$) at the equilibrium flotation temperature of the float in the latter ($t_2$).

In order to determine the deuterium concentration of the test material ($C_2$) on the basis of these results, it is necessary to know the density $t_1$ of the water taken as a standard. Its density is usually determined at 25°. Tables in which data is given on the density of deuterium oxide at various temperatures (see [1]) can be used for conversion to other temperatures if it is assumed that the density of heavy water with deuterium concentrations approximating to 100% change in the same way with temperature. When the deuterium concentration of the water used for calibration is 95%, and $t_1$ differs by 5° from 25°, such an assumption leads to an error in the determination of the density of the order of 0.00001, or to about 0.01 atom.% D in the determination of the concentration. Knowing the density of the test water at temperature $t_2$, it is possible, in a similar way to find its density at 25°, and, by dividing by the density of normal water at the same temperature ($d_4^{25} = 0.997075$ g/ml) to convert to $d_{25}^{25} = d_4^t / d_{4H_2O}$. From tables (see [1], appendix) it is then possible to find the deuterium concentration in the test water, and consequently, the deuterium concentration of the test material.

We shall illustrate the method of calculation, and the reproducibility of the results obtained by taking the analysis of deuteronaphthalene as an example.

$$t_1 = 21{,}7°; \quad d_{4\,(st)}^{25} = 1{,}10011; \quad C_1 = 95{,}93 \text{ at. } \%.$$

We determine

$$d_{4\,(st)}^{21.7°} = d_{4\,(st)}^{25} + [d_{4\,(D_2O)}^{21.7} - d_{4\,(D_2O)}^{25}] =$$

$$= 1{,}10011 + (1{,}10509 - 1{,}10446) = 1{,}10074.$$

$$t_2 = 27{,}2°; \quad d_{4(test)}^{27.2} = d_{4\,(st.)}^{21.7} = 1{,}10074.$$

We determine

$$d_{4(test)}^{25} = d_{4(test)}^{27.2} + [d_{4\,(D_2O)}^{25} - d_{4\,(D_2O)}^{27,\,2}] =$$

$$= 1{,}10074 + (1{,}10446 - 1{,}10396) = 1{,}10124.$$

$$d_{25(test)}^{25} = \frac{d_{4(test)}^{25}}{d_{4\,(H_2O)}^{25}} = \frac{1{,}10124}{0{,}99707} = 1{,}10447.$$

Using tables (see [1] p. 226) we find for $\Delta S_{25}^{25} = 0.10449$

$$C_2 = 96.99 \text{ atom.\%}$$

In a parallel analysis

$$t_2 = 27.1°, \; C_2' = 96.97 \text{ atom.\%}.$$

Control experiments in which 0.3 ml of heavy water of known isotopic composition was passed through the setup under our analytical conditions, showed that the equilibrium flotation temperature of the float changes by 0.1°, which corresponds to a change in deuterium concentration of ± 0.02 atom.%. During actual analysis the equilibrium flotation temperature was reproduced with the same accuracy. The error indicated above which is introduced during calculation lies within the limits of ± 0.01 atom.%. Accordingly, the method described permits determinations to be carried out with an accuracy of 0.05 atom%.

We used this method for establishing the conditions which affect the isotopic purity of deuteroammonia obtained from magnesium nitride and heavy water containing 99.6% $D_2O$ [3, 4]. It was found that when the deuteroammonia was prepared without observing any special precautions, its deuterium content did not exceed 95%. This low value for the deuterium concentration is a consequence of the fact that magnesium nitride reacts very readily with atmospheric moisture to form $Mg(OH)_2$ and $NH_3$. The $NH_3$ is adsorbed by the nitride. $Mg(OH)_2$, as shown experimentally, is capable under the conditions used for preparing $ND_3$ of exchanging with hydrogen, as a result of which the deuterium concentration drops.

When, however, the operation with magnesium nitride is carried out in a dry chamber, and, furthermore, when the nitride immersed in the cylinder used for preparing the ammonia, and evacuated beforehand on heating, is treated with small amount (1-2 ml) of liquid $ND_3$ which is used for desorbing the volatile ammonia from the surface of the $Mg_3N_2$ and the vessel, the latter having been pumped out before breaking the ampoule with the heavy water, then ammonia containing 98.6% D can be prepared.

## SUMMARY

A semi micro method for the isotopic analysis of materials containing about 100% of deuterium is described. For the determination 0.2-0.3 ml of water from the combustion of the test material is required. The method is based on measurement of the density of the water by means of a micro float. The accuracy of the method is 0.05 atom.%.

The method is used for the analysis of organic compounds containing about 100% deuterium, and deuteroammonia obtained by the interaction of $D_2O$ and $Mg_3N_2$.

## LITERATURE CITED

[1] A. I. Shatenshtein, E. A. Yakovleva, E. N. Zvyagintseva, Ya. M. Varshavskii, E. A. Izrailevich, and N. M. Dykhno, "Isotopic Analysis of Water," [in Russian] Izd AN SSSR, Moscow, 1957.

[2] A. I. Shatenshtein, J. Phys. Chem. 15, 246 (1941).

[3] G. S. Landsberg, A. I. Shatenshtein, G. V. Peregudov, E. A. Izrailevich, and L. A. Novikova, Optics and Spectroscopy, 1, 34 (1956).

[4] A. I. Shatenshtein, G. V. Peregudov, and E. A. Izrailevich, J. Phys. Chem. 32, 146 (1958).

[5] V. R. Kalinachenko, Ya. M. Varshavskii, and A. I. Shatenshtein, J. Phys. Chem. 30, 1140 (1956).

Received February 20, 1958

# DETERMINATION OF MICRO AMOUNTS OF XENON BY MEANS OF THE MASS SPECTROMETER

E. K. Gerling and Yu. A. Shukolyukov

Laboratory of Pre-Cambrian Geology, Acad. Sci. USSR, Leningrad

In carrying out the xenon method for the determination of the absolute age of minerals in actual practice [1], the basic problem is the isolation and measurement of micro amounts of xenon. Hitherto no method has been developed for the determination of small amounts ($10^{-6}$ – $10^{-5}$ $cm^3$) on this element. In this connection therefore we studied the possibility of using the MS-2M mass spectrometer for determination of xenon [2].

In order to calibrate the mass spectrometer, standards were prepared – mixtures of argon and xenon of known composition – in a high-vacuum setup schematically shown in Fig. 1. Traces of air were absorbed by keeping the argon and xenon over metallic calcium, first at 650° and subsequently at 300°. The amount of argon was measured in manometer 1. The same manometer served for the transfer of gases from one part of the setup to the other. Xenon was measured on the more sensitive manometer 2. Subsequent checks showed that the amount of argon present in the xenon used was about 1%.

Four pairs of standard mixtures were prepared: 1) 0.94% Xe and 0.095% Xe, 2) 0.29% Xe and 0.13% Xe, 3) 0.94% Xe and 0.26% Xe, 4) 1.18% Xe and 0.18% Xe. Results obtained with various standards coincided within the experimental error.

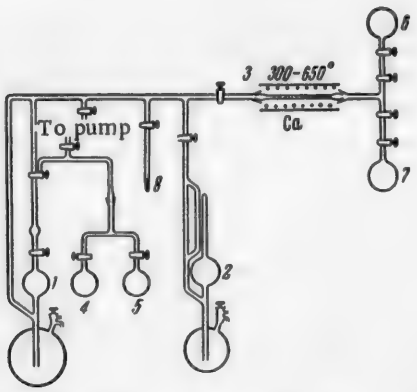



Fig. 1. High-vacuum setup: 1 and 2) McLeod gauges; 3) metallic calcium; 4 and 5) vessels for standards and control mixtures; 6) vessel containing argon; 7) vessel containing xenon; 8) activated carbon.

Using the mass spectrometer, determinations were carried out of the xenon content of control mixtures of varying composition prepared beforehand (Table 1).

The control mixtures were prepared in the same setup as the standards.

During the separation of xenon from minerals, one of the operations is the adsorption of the gases by means of cooled activated charcoal and subsequent desorption of the gases [1]. Accordingly, the control mixtures were also adsorbed with activated charcoal at -183° before carrying out measurements on the mass spectrometer.

In the course of the work it was established that during desorption from the activated charcoal of the mixture of argon and xenon, there occurs partial separation of these gases. Xenon is held very firmly by the charcoal, so that some of it still remains adsorbed even at a temperature of 320°.

In an experiment where 10 g of activated charcoal was used, about 30% of the amount of xenon taken remained adsorbed. When using 0.1 g of charcoal at a temperature 320°, 10-12% of the xenon was not desorbed.

Only by decreasing the weight of the adsorbent to 0.04 g was it found possible to desorb all the xenon completely.

Moreover, it was observed that partial adsorption of the xenon occurs in the traps cooled with liquid air. 20-30% of the amount of xenon could be held on the trap walls, accordingly, before admitting the samples into the mass spectrometer; a trap containing a mixture of alcohol and dry ice (temperature −78.5°) was used for freezing the vapors.

TABLE 1

| Xe taken, $cm^3 \cdot 10^{-5}$ | Xe found, $cm^3 \cdot 10^{-5}$ | | | Deviation of the mean value found from that actually taken, % | Xe taken, $cm^3 \cdot 10^{-5}$ | Xe found, $cm^3 \cdot 10^{-5}$ | | | Deviation of the mean value found from that actually taken, % |
|---|---|---|---|---|---|---|---|---|---|
| | pressure method | method of relative sensitivities | by the two methods | | | pressure method | method of relative sensitivities | by the two methods | |
| 0,342 | 0,314 | 0,328 | 0,321 | − 6 | 1,82 | 2,06 | 1,97 | 2,03 | +12 |
| 0,470 | 0,446 | 0,470 | 0,458 | − 3 | 1,90 | 1,47 | 1,50 | 1,49 | −21 |
| 0,505 | 0,616 | 0,500 | 0,558 | +12 | 1,90 | 2,00 | 2,05 | 2,02 | + 6 |
| 0,531 | 0,504 | 0,531 | 0,517 | − 3 | 2,29 | 2,43 | 2,50 | 2,46 | + 7 |
| 0,609 | 0,469 | 0,609 | 0,539 | −12 | 2,36 | 2,18 | 2,60 | 2,39 | + 1 |
| 0,905 | 0,886 | 0,751 | 0,816 | −10 | 2,67 | 2,78 | 2,78 | 2,78 | + 4 |
| 0,914 | 1,28 | 0,940 | 1,11 | +10 | 3,28 | 2,85 | 2,79 | 2,82 | −14 |
| 1,51 | 1,72 | 1,42 | 1,57 | + 3 | 4,54 | 4,84 | 4,54 | 4,69 | + 3 |
| 1,57 | 1,53 | 1,51 | 1,52 | − 3 | 4,85 | 4,85 | 4,75 | 4,80 | − 1 |
| 1,62 | 1,78 | 1,52 | 1,65 | + 2 | | | | | |

A tube containing heated calcium metal was fitted into the admittance system of the mass spectrometer, so that any possible small ingress of air could not affect the results.

Two methods of measurement on the mass spectrometer were used: the pressure method and the method of relative sensitivities.

### The Pressure Method

After establishing a pressure of $1 \times 10^{-7} - 2 \times 10^{-7}$ mm Hg in the mass spectrometer, the apparatus was adjusted to the xenon isotope with a mass of 132. The form of the relation between the intensity of the peak and the pressure in the region of the ionic source was determined for two standard mixtures with different xenon contents. The pressure p was measured on the standard ionization manometer of the mass spectrometer. Curves

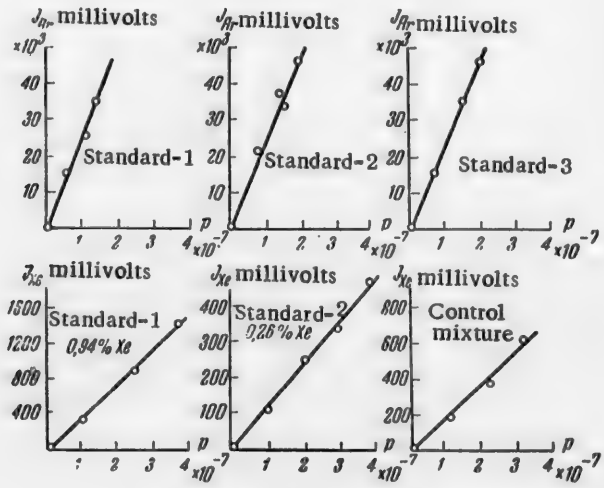



Fig. 2. Calibration curves.

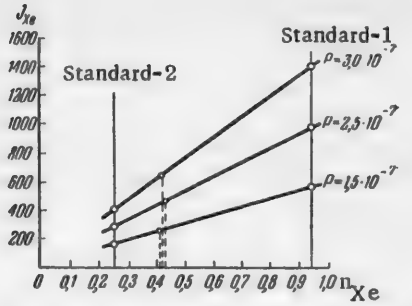



Fig. 3. Determination of xenon in mixtures: $n^{x}_{Xe}$ = 0.4, 0.42, 0.41; average 0.42 $V^{x}_{Xe} = \frac{0.42 \cdot 4.84 \cdot 10^{-3}}{100} =$ $2.04 \cdot 10^{-5}$ $cm^3$ Xe.

of $J_{Xe} = f(p)$ were constructed for both standards, where $J_{Xe}$ is the intensity of the peak in mv, p is the pressure in the ionic source and n is the percentage content of the mixture. As a rule, the peak intensity was proportional to the pressure in the region of the ionic source. Only for $p > 5 \times 10^{-7}$ mm Hg did the linear relation break down. As an illustration we have given curves (Fig. 2. and 3) which were obtained in one of the experiments ($4.84 \times 10^{-3}$ $cm^3$ Ar and $1.90 \times 10^{-5}$ $cm^3$ Xe).

From the results obtained, calibration curves $n^{x}_{Xe} = f(J_{Xe})_p$ = const. were constructed for several pressures.

The values of the peak intensity $Xe^{132}$ were then measured for the test mixtures at various pressures p. Curves $J_{Xe} = f(p)_x$ were constructed. Using these results and the calibration straight lines, it is possible to find the mean value $n^{x}_{Xe}$ the percentage content of xenon in the test mixture (Fig. 3).

Construction of the curves is not obligatory nevertheless we thought it was more convenient to adopt a graphical method of calculation, since any deviation from the proportional relationship will not escape observation in this case.

### The Relative Sensitivity Method

The sensitivity of the mass spectrometer to argon and xenon is determined by means of the standard mixtures:

$$\Delta J_{Ar}/\Delta P_1 = S_{Ar} \quad \Delta J_{Xe}/\Delta P_2 = S_{Xe} \cdot n_{Xe}/n_{Ar}.$$

Here, $\Delta J_{Ar}/\Delta P_1$ and $\Delta J_{Xe}/\Delta P_2$ are the changes in intensity on changing the pressure in the ionic source by $1 \times 10^{-7}$ mm Hg, where $\Delta J_{Xe} = \Delta J^{132}_{Xe}/N$, N being the fraction of the $Xe^{132}$ isotope in the mixture of xenon isotopes; S is the sensitivity; $n_{Xe}$ and $n_{Ar}$ are the percentage contents in the standard mixtures. From these it is easy to find the relative intensity:

$$\frac{\Delta J_{Ar} \cdot \Delta P_2}{\Delta P_1 \cdot \Delta J_{Xe}} = \frac{S_{Ar}}{S_{Xe}} \cdot \frac{n_{Ar}}{n_{Xe}}, \quad K = \frac{S_{Ar}}{S_{Xe}} = \frac{\Delta J_{Ar} \cdot \Delta P_2 \cdot n_{Xe}}{\Delta J_{Xe} \cdot \Delta P_1 \cdot n_{Ar}}.$$

Here K is the relative intensity which indicates how many times the sensitivity of the mass spectrometer towards argon is less than its sensitivity to xenon. The value of K was determined separately in each experiment on the basis of both standard mixtures. Usually, the relative sensitivity was about 0.5 and changed somewhat with the adjustment of the apparatus. Accordingly, it was found essential to carry out the measurements as rapidly as possible and without any changes in the adjustment (tuning) of the mass spectrometer.

Knowing the value of K and $\Delta J_{Ar} \cdot \Delta P_2 / \Delta J_{Xe} \cdot \Delta P_1$ for the test mixture, it is possible to find its percentage content of xenon:

$$\frac{n_{Ar}}{n_{Xe}} = \frac{1}{K} \cdot \frac{\Delta P_2 \cdot \Delta J_{Ar}}{\Delta P_1 \cdot \Delta J_{Xe}}; \quad \frac{100 - n_{Xe}}{n_{Xe}} = \frac{1}{K} \cdot \frac{\Delta P_2 \cdot \Delta J_{Ar}}{\Delta P_1 \cdot \Delta J_{Xe}}.$$

$$\text{From which } n_{Xe} = 100 \Big/ \left( \frac{1}{K} \cdot \frac{\Delta P_2 \cdot \Delta J_{Ar}}{\Delta P_1 \cdot \Delta J_{Xe}} + 1 \right).$$

In practice the experimental determination of the values of $\Delta J_{Ar}/\Delta P_1$ and $\Delta J_{Xe}/\Delta P_2$ for the control and standard mixtures permitted calculations to be made according to both methods.

As an example we have given below the calculation of the xenon content on the basis of the experimental results given above (Figs. 2 and 3).

The value of K is determined:

$$\text{from standard} \quad -1: K = \frac{47\,000 \cdot 4 \cdot 10^{-7} \cdot 0{,}94}{2 \cdot 10^{-7} 1600 \cdot 99{,}06} = 0{,}555$$

$$\text{from standard} \quad -2: K = \frac{50\,000 \cdot 3 \cdot 10^{-7} \cdot 0{,}26}{2 \cdot 10^{-7} \cdot 335 \cdot 99{,}74} = 0{,}585$$

The mean value of K = 0.570 ± 0.015.

Next, we find $n^{x}_{Xe}$:

$$n^{x}_{Xe} = 100\left(\frac{1 \cdot 48\,000 \cdot 3 \cdot 10^{-7}}{0{,}57 \cdot 2 \cdot 10^{-7} \cdot 530} + 1\right) = \frac{100}{242} = 0{,}41\ \%.$$

Converting to amounts by volume, we get:

$$\frac{4{,}84 \cdot 10^{-3} \cdot 0{,}41}{100} = 1{,}88 \cdot 10^{-5}\ \text{cm}^3.$$

All the results obtained are given in Table 1. The deviation of the mean amount of xenon actually found from that taken amounts to ±8%. The accuracy of both methods of measurement proved to be approximately the same.

An additional check on the reliability of the results obtained was a determination of the xenon content of uraninite from Chernaya Salma which we carried out. The xenon content of this sample had been determined earlier by the usual volumetric method ([1]. The results obtained by both methods were found to be in good agreement with each other; this testifies to the reliability of the method suggested above for the determination of micro amounts of xenon (Table 2).

TABLE 2

| Method | Sample wt., g | Amounts of xenon per gram of mineral, $cm^3$ |
|---|---|---|
| Mass spectrometric | 11.4 | $(0.75 \pm 0.12)\ 10^{-6}$ |
| Volumetric | 350 | $(0.77 \pm 0.06)\ 10^{-6}$ |

It follows from this work that:

During the quantitative determination of xenon, measures should be taken to prevent loss of xenon as the result of adsorption.

Using a mass spectrometer, it is possible to determine $1 \times 10^{-6} - 5 \times 10^{-5}$ $cm^3$ of xenon with a mean accuracy of ±8%.

The accuracy of the pressure method and the method of relative sensitivity is approximately the same.

## SUMMARY

Reference and control mixtures of argon and xenon with a definite content of xenon have been prepared by means of a vacuum apparatus. A MS-2M mass spectrometer has been used for determining about $10^{-5} - 10^{-6}$ $cm^3$ of xenon in the control mixtures.

Two methods have been used: the pressure method and the method of relative sensitivity. A mixture of solid $CO_2$ and ethanol (−78.5°) was used instead of liquid oxygen in the vacuum traps, so as to prevent loss of xenon resulting from absorption. Loss of xenon on account of the difficulty of desorbing it from the activated charcoal was overcome by using small amounts of adsorbent (0.04 g). The mean experimental accuracy for the determination of $10^{-5} - 10^{-6}$ $cm^3$ of xenon is ± 8%. The radiogenic xenon content of Black Salma uraninite has also been determined. The value obtained by the mass-spectrometric method ($0.75 \times 10^{-6}$ $cm^3/g$) was found to be in good agreement with that obtained by a volumetric method ($0.77 \times 10^{-6}$ $cm^3/g$).

## LITERATURE CITED

[1] V. G. Khlopin, E. K. Gerling, and N. V. Baranovskaya, Bull. Acad. Sci. USSR, Chem. Sci. Div. No. 6, 599 (1947).

Received November 25, 1957

# CONDUCTOMETRIC ANALYSIS OF NATURAL WATERS, COMMUNICATION 2. DETERMINATION OF MAGNESIUM AND ANIONS*

G. B. Pasovskaya

Turkmen Medical Institute, Ashkhabad

## Determination of Magnesium

In recent years a large amount of work has been published on the use of Complexon III for analytical purposes. Among the papers which have appeared are ones devoted to the complexonometric determination of magnesium in water [1-2]. Nevertheless, the complexonometric method of determining magnesium in colored and turbid water is difficult, and is often impossible because of the difficulty of establishing the color change of the indicator. Moreover, iron, when present in the test water in amounts greater than 10 mg/liter, also interferes. Calcium, just like magnesium, forms with Complexon III at pH 10, a stable compound, readily soluble in water, so that calcium, too, interferes with magnesium determination. Mannite [3] or ammonium oxalate [1] has been recommended for preventing interference by calcium. In the method which we have developed calcium was precipitated with oxalate**; the suspension obtained was titrated with a solution of Complexon III. Belcher and Wilson [4] indicate that magnesium hardness can be determined after precipitation of the calcium with a soluble oxalate. Titration can be carried out in the presence of the precipitated calcium oxalate.

The suggested method was worked out using synthetic mixtures made up from standard solutions of 0.1 N calcium chloride and 0.1 N magnesium sulfate; the applicability of the method in the presence of large amounts of aluminum and iron was established.

It was found that aluminum and iron, given in large amounts (100 mg/liter), do not interfere. On addition of sodium oxalate to test solutions containing aluminum and iron, there are formed oxalate compounds which are soluble in water, and which are broken down on addition of an ammoniacal buffer solution (pH 10), since they are unstable in an alkaline medium; under these conditions therefore the hydroxides of these metals are formed, and they do not interfere with the process of conductometric titration.

Apparatus. A vessel fitted with a cylindrical piston stirrer was used for conductometric titration [6]. The reagent was added by means of a pneumatic microburet [7]. Titration was carried out on an apparatus of the Toropov system [8].

The 0.1 N solution of Complexon III was standarized by means of a standard mixture of 0.01 N solutions of calcium chloride *** and magnesium sulfate**** taken in the ratio of 3 : 1 by volume, and prepared by

*For Communication 1, see Bull. Acad. Sci. Tadzh. SSR.

**Sodium oxalate was chosen as the reagent, since sodium ions have a lower mobility than potassium and ammonium ions.

***5.005 g of calcium carbonate (chemically pure grade dried at 110° for 1 hour and cooled in a desiccator over calcined calcium chloride) was dissolved in the minimum amount of concentrated hydrochloric acid contained in a liter standard flask. Whe solution was complete the volume of the contents of the flask was made up to the mark with distilled water and thoroughly mixed.

****12.325g of chemically pure grade magnesium sulfate containing seven molecules of water was dissolved in water in a liter standard flask and the volume made up to the mark with distilled water; the whole was then thoroughly mixed. The concentration of the solution thus obtained was checked [5], and, when necessary, a correction applied for the normality.

mixing the 0.1 N solutions.

25 ml of the standard mixture (calcium : magnesium = 3 : 1) was pipetted into a 50 ml beaker, and 1 drop of Methyl Red and 0.1 N hydrochloric acid added to the appearance of a rose color. The solution was boiled on an electric hot plate and evaporated to a volume of 5-10 ml; the solution was then cooled to 80° and 1 drop of a saturated solution of sodium oxalate added to it, followed by dropwise addition, with stirring, of 0.5 ml of an ammoniacal buffer mixture with a pH of 10 (0.1 N $NH_4OH$ and 0.1 N $NH_4Cl$ mixed in the proportion of 1 : 5). After cooling to room temperature the solution was quantitatively transferred to the titration vessel, and its volume made up to 50 ml; it was finally conductometrically titrated with Complexon III. From the amount of Complexon III used up in the titration the number of mg of magnesium corresponding to 1 ml of titrant was calculated.

For determination of the magnesium content of natural water, 5-25 ml of the test water, depending on the expected magnesium content, was measured into a 50 ml beaker. One drop of Methyl Red was added to the solution; this was followed by addition of 0.1 N hydrochloric acid until the color of the indicator had turned to rose. The solution was heated on an electric hot plate (when the color of the indicator changed to yellow some more 0.1 N hydrochloric acid was added to change the color back to rose* again) and the procedure outlined above then followed.

From the amount of 0.1 N Complexon III solution used up, the magnesium content of the test sample was then calculated.

The applicability of the method was checked on natural waters, the magnesium content of which was determined by the method suggested, and by the pyrophosphate method [9], using the filtrate obtained after removal of calcium by the oxalate method. The results obtained, which are given in Table 1, show that the suggested method can be used for the determination of magnesium in natural waters.

TABLE 1

Determination of Magnesium in Natural Waters

| $Ca^{2+}$ content of the water, mg/liter | Conductometric determination | | Gravimetric determination | |
|---|---|---|---|---|
| | water taken, ml | $Mg^{2+}$ found, mg/liter | water taken, ml | $Mg^{2+}$ found, mg/liter |
| 28,27 | 25 | 16,95 | 1000 | 16,98 |
| 43,61 | 25 | 19,44 | 1000 | 19,42 |
| 56,54 | 10 | 33,61 | 1000 | 33,91 |
| 83,92 | 10 | 43,21 | 1000 | 43,78 |
| 76,09 | 10 | 48,62 | 1000 | 48,99 |
| 95,64 | 10 | 62,42 | 1000 | 62,90 |
| 141,10 | 5 | 72,02 | 1000 | 72,70 |

## Determination of Anions

Usually, during the analysis of natural waters, sulfate, chloride, and bicarbonate are determined. In this connection, therefore, a method has been developed for the conductometric analysis of natural waters for these anions on the basis of a technique described earlier [6-8, 10].

Determination of Sulfates. Test water containing 2-10 mg of sulfate was measured into the titration vessel. 1-2 drops of Methyl Red was added to the solution followed by 0.1 N hydrochloric acid to give a neutral reaction. Dry, ground-up barium sulfate (about 100 mg) was then added, followed by 0.5 ml of a saturated solution of Methyl Violet. The solution was then mixed and 0.5 ml of a standard solution of 0.1 N barium chloride (12.21 g $BaCl_2 \cdot 2H_2O$ in 100 ml water) measured out with a micropipet added; the volume was finally made up to 100 ml with water. The solution was thoroughly mixed and excess barium chloride titrated conductometrically with 1 N sodium sulfate solution (standardized conductometrically against $BaCl_2$).

*Excess acid must be avoided.

Determination of chlorides. Test water containing 2-20 mg of chloride was measured out into the titration vessel. One drop of Methyl Red was added, followed by 1 N nitric acid until the solution was neutral, 2-3 drops of nitric acid in excess was then added. The solution was mixed and water added to bring the volume up to 25 ml, the solution was conductometrically titrated with 0.5 N mercuric nitrate (8.340 g of mercuric nitrate was dissolved in water contained in a 100 ml standard flask and conductometrically standardized against 0.1 N potassium chloride). When, on addition of reagent there was observed the appearance of a yellow turbidity, the test had to be prepared again by adding to it, after neutralization, 6-7 drops of nitric acid.

Determination of carbonate hardness. a) Determination of carbonate hardness in the absence of phosphates. Test water containing 0.2-0.02 mg. equivalents of carbonate was measured into the titration vessel. 100 mg of dry barium chloride was added, followed by 5 ml of 0.01 N hydrochloric acid and 5 ml of 0.01 N acetic acid. When iron was present, sodium fluoride was added until the solution was decolorized, or the acetic acid was substituted by 50 mg of citric acid. The volume of the mixture was adjusted to 50 ml with distilled water and the solution conductometrically titrated with 0.1 N $Ba(OH)_2$ (standardized conductometrically with 0.01 N HCl).

b) Determination of carbonate hardness in the presence of phosphates. For removal of phosphates the test water was measured into a 50 ml beaker and 5 ml of 1% barium chloride solution added. After 2-3 minutes, when the precipitate had settled out, the solution was filtered through a filter of the minimum possible size into the titration vessel. The beaker in which precipitation had been carried out was rinsed three times with 1 ml lots of cold water which was then poured through the same filter each time. Finally the precipitate on the filter was washed with pure distilled water and the filtrate obtained titrated as described above.

Determination of total hardness. Test water containing 0.06-0.03 mg · equivalents of calcium and magnesium was measured into a 50 ml flask. One drop of Methyl Red was added, followed by hydrochloric acid until the color of the solution was red. The solution obtained was boiled on an electric hot plate for several minutes. When the color of the solution changed during the boiling process, some more hydrochloric acid was added.

The solution was cooled to room temperature under tap water, and quantitatively transferred to the titration vessel; distilled water was added to bring the volume up to 50 ml and 0.5 ml of a buffer solution with pH 10* added. The solution prepared in this way was mixed and titrated conductometrically with 0.1 N Complexon III solution.

TABLE 2

Analysis of Natural Waters for Anions and Hardness by Classical and Conductometric Methods

| Method | $SO_4^{2-}$, mg/liter | $Cl^-$, mg/liter | Carbonate hardness, mg · equivalents | Total hardness, mg · equivalents |
|---|---|---|---|---|
| Conductometric | 56,40 | 20,39 | 3,01 | 3,85 |
| Classical | 57,5 | 20,2 | 2,95 | 3,86 |
| Conductometric | 239,96 | 107,64 | 6,22 | 9,99 |
| Classical | 240,4 | 107,74 | 6,20 | 10,00 |
| Conductometric | 399,3 | 266,2 | 2,20 | 7,79 |
| Classical | 400,5 | 266,0 | 2,18 | 7,76 |
| Conductometric | 599,90 | 84,78 | 10,83 | 17,3 |
| Classical | 601,5 | 84,3 | 10,8 | 17,28 |

The method suggested has been checked on natural waters; analysis was carried out by generally accepted methods and by the suggested methods. The results obtained are given in Table 2.

It is clear from these results that the method suggested can be used for mass analyses of water.

*The buffer solution was added last in order to avoid precipitation of magnesium hydroxide from water containing large amounts of magnesium.

## SUMMARY

A rapid conductometric method has been developed for the determination of magnesium, anions, and hardness in natural, turbid, and colored waters.

## LITERATURE CITED

[1] Z. V. Arkhangel'skaya, Industrial Labs. 20, 4 (1954).

[2] A. De Souse, Anal. Abst. No. 2, 251 (1954).

[3] R. M'yuraki, Ref. Chem. J. No. 22, 228 (1955)

[4] R. Belcher and C. L. Wilson, New Methods in Analytical Chemistry, Second Printing, 196 (1956).

[5] Instructions for the Determination of Water Hardness by a Complexonometric Method. USSR Ministry of Chemical Industry. Glavkhimreaktiv. Voikov State Chem. Factory, Moscow, 1952 [in Russian].

[6] A. P. Toropov, Trans. Central Asian Inst. 33, 99, 1952.

[7] G. B. Pasovskaya, Bull. Acad. TSSR, 4, 35 (1955).

[8] A. P. Toropov and G.B. Pasovskaya, J. Anal. Chem. 12, 328 (1957).*

[9] L. M. Kolthoff and E. B. Sandell, "Quantitative Analysis," Goskhimizdat, 1948, p. 987. **

[10] A. P. Toropov and G. B. Pasovskaya, Trans. Central Asian Inst. 28, 75 (1951).

Received June 29, 1957

*Original Russian pagination. See C.B. Translation.

**Russian translation.

# ELEMENTAL ORGANIC ANALYSIS BY THE "WET COMBUSTION METHOD"

A. P. Terent'ev and B. M. Luskina

The M. V. Lomonosov Moscow State University

Analysis of organic compounds using the technique of complete oxidation by means of oxidizing agents in solution is called the wet combustion method. Kjeldahl determination of nitrogen is of this type. Similar methods have been known for a long time and are often used for decomposing organic materials with the aim of determining one element. Such methods are only rarely used for the simultaneous determination of several elements. The first to indicate such a possibility during the analysis of organometallic compounds was Messinger in 1888 [1].

The oxidizing agent used most frequently is chromic acid or its salts mixed with concentrated sulfuric acid or mixed with sulfuric and phosphoric acids. Houghton [2] and Van Slyke [3] have given literature reviews.

As a rule, it is necessary to carry out "complete combustion"; for this purpose, the gaseous reaction products are usually passed through a heated tube containing cupric oxide. Nevertheless, this method has a number of essential drawbacks. In particular, the greatest difficulties arise during the determination of halogen-containing materials [4].

In the technique we wish to propose the catalyst which we used for complete combsution was chromic oxide. This enabled us to avoid a number of difficulties.

Fedoseev and Pavlenko [5] used chromic oxide as a catalyst for surface combustion during elemental analysis. Klimova, Korshun, and Bereznitskaya [6] have used it during microelemental analysis of organosilicon compounds.

The combined combustion method which has been developed, and which can be called the chromic method, is of great interest, particularly for production laboratories. Obviously, direct determination of hydrogen, sulfur, and chromium is impossible, but, on the other hand, the method does permit simultaneous determination of many other elements, in addition to carbon and nitrogen, on one aliquot. Using this technique, it is possible to analyze not only dry materials, but also solutions of organic compounds in water or sulfuric acid. The simplicity of the apparatus, and the possibility of working with aliquots over a wide range, makes the method very attractive.

Determination of carbon. The oxidation mixture which we use consists of concentrated sulfuric acid and a concentrated aqueous solution of chromic acid, which is gradually added in small portions during the oxidation process. For ensuring complete combustion, specially prepared chromic oxide deposited on lumps of pumice was used. Combustion of the aliquot of organic test materials is carried out in the apparatus shown in the diagram.

10 ml of concentrated sulfuric acid is placed in the reaction flask 3, while 1-2 ml of chromic acid is placed in the side tube of this vessel. A stream of oxygen is then passed through at the rate of about 50-60 ml/ /minute, and the tared tube 11 connected; by lifting the stopper a little beaker containing the test aliquot is then lowered into the reaction flask. The chromic acid is added from the side-tube dropwise, the reaction flask

being rotated carefully around joint 6 which is greased, like joints a and b, with phosphoric acid. The flask is immersed in a bath heated to 150-160°. The gaseous reaction products, which may contain some products of incomplete combustion (CO, $CH_3COOH$, etc.), together with the hydrogen stream pass into the heated tube (700-750°) containing chromic oxide, here combustion is completed; the final oxidation products then pass

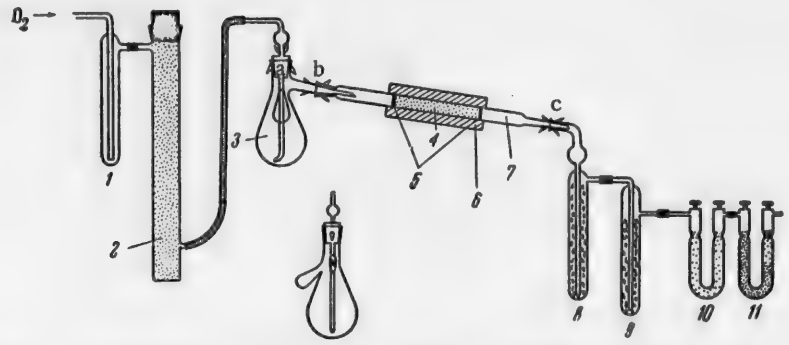



Fig. 1. Wet combustion apparatus: 1) Bubble counter filled with concentrated sulfuric acid; 2) ascarite column for drying the oxygen; 3) reaction flask; 4) catalyst, 80 mm long; 5) loose stopper of asbestos; 6) electric oven at 700-750°; 7) quartz tube 200 mm long and 10-12 mm in diameter; 8) vessel containing glass rods (a plug of glass wool is placed in the bulb) moistened with an acetic acid solution of hydrazine hydrate; 9) vessel containing glass rods moistened with concentrated sulfuric acid; 10) tube containing Anhydrone 11) tube containing ascarite and Anhydrone.

through flask 8 (the purpose of which is indicated below), through concentrated acid 9, and Anhydrone 10 for purifying and drying the $CO_2$ formed. Carbon is determined from the increase in weight of tube 11 which is filled with ascarite and Anhydrone. Tube 12 containing the same packing is connected to tube 11 (12 is not shown in the diagram). Combustion does not take longer than 30 minutes.

TABLE 1

Determination of Carbon

| Test material | Sample wt., mg | $CO_2$, mg | C, % found | C, % calc. | Difference |
|---|---|---|---|---|---|
| Salicylic acid $C_7H_6O_3$ | 110,80 | 245,99 | 60,59 | | —0,28 |
| | 70,94 | 158,24 | 60,88 | 60,87 | +0,01 |
| Ethylanthraquinone $C_6H_{12}O_2$ | 60,81 | 181,54 | 81,48 | | +0,14 |
| | 59,84 | 178,63 | 81,47 | 81,34 | +0,13 |
| Acenaphtnene $C_{12}H_{10}$ | 54,43 | 186,97 | 93,75 | | +0,29 |
| | 54,22 | 186,03 | 93,63 | 93,46 | +0,17 |
| Cholesterol $C_{27}H_{46}O$ | 53,68 | 164,68 | 83,72 | | —0,15 |
| | 60,12 | 184,74 | 83,86 | 83,87 | —0,01 |
| Xanthone $C_{13}H_8O_2$ | 49,82 | 145,02 | 79,44 | | —0,14 |
| | 52,38 | 152,83 | 79,63 | 79,58 | +0,05 |
| Diethyl ester of dimethylbenzodifurane dicarboxylic acid $C_{18}H_{18}O_6$ | 64,84 | 155,64 | 65,51 | 65,45 | +0,06 |
| | 60,59 | 145,68 | 65,62 | | +0,17 |

Simultaneous determination of carbon and other elements can be carried out in the same apparatus. Modifications to the technique are only necessary in the case of combustion of chlorine-containing materials.

Simultaneous determination of carbon and chlorine (or bromine). During the oxidation of chlorine-containing organic materials by the chromic method, formation of volatile chromyl chloride occurs; when the latter passes into the tube containing chromic oxide, it is decomposed to liberate chlorine, oxygen, and to form chromic oxide. Chromyl chloride is also partially decomposed by water vapor with formation of hydrogen chloride. The cupric oxide used earlier, forms, in this case, volatile chloride compounds. Bromine-containing organic materials are oxidized with formation of elemental bromine.

A solution of hydrazine hydrate neutralized with acetic acid to a pH of 6 is used for absorption of the halogens. Under these conditions the halogens are completely absorbed while the $CO_2$ is not absorbed.

The aliquots of halogen-containing materials are subjected to combustion in the same way as that described for the determination of carbon. During the analysis of chlorine-containing compounds, the amount of chromic acid taken is 1-2 ml more, and it is added gradually dropwise before starting to heat, addition being carried out as the red-brown fumes of chromyl chloride are driven out of the flask; about a third of the amount of chromic acid taken is left in the side tube. Flask 3 is then immersed in the heated bath so that the side tube of the flask touches the liquid in the bath. This ensures that the chromyl chloride deposited on the flask walls is decomposed by water vapor. The halogens are absorbed in vessel 8 containing glass rods moistened with the acetic acid solution of hydrazine hydrate (pH 6). The remaining operations are the same as those described for the determination of carbon. The chloride or bromide ions contained in vessel 8 are titrated by the Volhard method.

TABLE 2

Simultaneous Determination of Carbon and Chlorine (or Bromine)

| Test material | C, in % | | Difference | Hal, in % | | Difference |
|---|---|---|---|---|---|---|
| | found | calc. | | found | calc. | |
| p-Chlorobenzoic acid $C_7H_5O_2Cl$ | 53,50<br>53,57 | 53,70 | —0,20<br>—0,13 | 22,44<br>22,54 | 22,65 | —0,21<br>—0,11 |
| 2,6-Dichloroquinone $C_6H_2O_2Cl_2$ | 40,61<br>40,82 | 40,72 | —0,11<br>+0,10 | 39,96<br>40,10 | 40,06 | —0,10<br>+0,04 |
| p-Nitrochlorobenzene $C_6H_4O_2NCl$ | 45,83<br>45,62 | 45,74 | +0,09<br>—0,12 | 22,44<br>22,35 | 22,50 | —0,06<br>—0,15 |
| 4-Chloro-5-methyl-2-isopropylphenol $C_{10}H_{13}OCl$ | 64,93<br>65,12 | 65,04 | —0,11<br>+0,08 | 19,35<br>19,25 | 19,20 | +0,15<br>+0,05 |
| Dinitrochlorobenzene. $C_6H_3O_4N_2Cl$ | 35,38<br>35,67 | 35,58 | —0,20<br>+0,09 | 17,34<br>17,56 | 17,50 | —0,16<br>+0,06 |
| 2,3-Dibromo-4-naphthaquinone $C_{10}H_4O_2Br_2$ | 38,24<br>38,32 | 38,01 | +0,23<br>—0,31 | 50,51<br>50,31 | 50,58 | —0,07<br>—0,27 |
| 2-Bromo-1,4-naphthaquinoneacetoacetic ester $C_{16}H_{13}O_5Br$ | 52,74<br>52,69 | 52,62 | —0,12<br>+0,07 | 22,06<br>21,83 | 21,88 | +0,18<br>—0,05 |
| Bromonitrobenzene $C_6H_4O_2NBr$ | 35,59<br>35,79 | 35,67 | —0,08<br>+0,12 | 39,40<br>39,60 | 39,56 | —0,16<br>+0,04 |

Thus, the use of chromic oxide as a catalyst for ensuring complete combustion, together with the use of an acetic acid solution of hydrazine hydrate for absorption of the halogens, make it possible to carry out simultaneous determination of carbon and chlorine (or bromine).

During the analysis of materials for their contents of carbon, or of carbon and halogen, it is possible to carry out combustion of two or even three aliquots in the same flask. For this purpose, the reaction flask is not disconnected and the sulfuric acid is not changed, the only additional operation is the addition of more chromic acid and a further aliquot of test material.

Simultaneous determination of carbon, chlorine, and nitrogen. When the nitrogen-containing compound gives ammonia in concentrated sulfuric acid, then nitrogen can be determined in the material as well as carbon and chlorine. For this purpose the contents of the reaction vessel 3, after combustion, is transferred to a

Kjeldahl flask excess alkali is then added and the ammonia is distilled over in the usual apparatus into a standard acid solution. In this way it is possible to determine nitrogen in amines, nitriles, pyrrolidines, indoles, etc.

TABLE 3

Simultaneous Determination of Carbon, Chlorine, and Nitrogen

| Test material | C, % | | Difference | Cl, % | | Difference | N, % | | Difference |
|---|---|---|---|---|---|---|---|---|---|
| | found | calc. | | found | calc. | | found | calc. | |
| Ester of o-hydroxybenzoic acid and the hydrochloride of N-ethyl-α-methylpyrrolidine $C_{14}H_{20}O_3NCl$ | 58,61 | 58,85 | −0,24 | 12,18 | 12,41 | −0,23 | 4,90 | 4,90 | 0,0 |
| | 58,87 | | +0,02 | 12,25 | | −0,16 | 5,06 | | +0,16 |
| The ester of cinnamic acid and the hydrochloride of N-ethyl-α-methylpyrrolidine $C_{16}H_{22}O_2NCl$ | 65,00 | 64,96 | +0,04 | 11,87 | 11,98 | −0,11 | 4,69 | 4,74 | −0,05 |
| | 64,88 | | −0,08 | 11,82 | | −0,16 | 4,83 | | +0,09 |
| The naphthyl ester of the hydrochloride of N-propyl-α-methylpyrrolidine $C_{18}H_{24}O_2NCl$ | 67,26 | 67,17 | +0,09 | 11,25 | 11,02 | +0,23 | 4,52 | 4,38 | +0,17 |
| | 67,11 | | −0,06 | 11,20 | | +0,18 | 4,49 | | +0,14 |
| Ethyl oxamate $C_4H_7O_3N$ | 41,30 | 41,02 | +0,28 | | | | 12,25 | 11,96 | +0,29 |
| | 41,03 | | +0,01 | | | | 11,99 | | +0,03 |
| Dinitrylsuccinic acid $C_4H_2N_2$ | 61,46 | 61,53 | −0,07 | | | | 35,84 | 35,88 | −0,04 |
| | 61,78 | | +0,25 | | | | 36,01 | | +0,13 |
| 1-Phenyl-2-methyl-3-carbethoxy-5-acetoxyindole $C_{20}H_{19}O_4N$ | 71,42 | 71,20 | +0,22 | | | | 4,00 | 4,15 | −0,15 |
| | 71,49 | | +0,29 | | | | 4,25 | | +0,10 |

TABLE 4

Simultaneous Determination of Carbon and Nitrogen in Compounds Containing Two forms of Nitrogen ("oxidizing" and "reducing")

| Test material | C, % | | Difference | N*, % | | Difference |
|---|---|---|---|---|---|---|
| | found | calc. | | found | calc. | |
| 3-Methyl-4-cyanoethyl-pyrazolone-5 $C_7H_9ON_3$ | 55,62 | 55,62 | 0,0 | 9,41 | 9,26 | +0,15 |
| | 55,61 | | −0,01 | 9,44 | | +0,18 |
| 1-Cyanoethyl-3-isobutyl-pyrazolone-5 $C_{10}H_{15}ON$ | 62,42 | 62,15 | +0,27 | 7,30 | 7,25 | +0,05 |
| | 62,24 | | +0,09 | 7,22 | | −0,03 |
| 1-Phenyl-3-methyl-4-cyanoethylpyrazolone-5 $C_{13}H_{13}ON_3$ | 68,67 | 68,70 | −0,03 | 6,30 | 6,16 | +0,14 |
| | 68,78 | | +0,08 | 6,15 | | −0,01 |
| The tricyanoethyl ester of trimethylol nitromethane $No_2 \cdot C(CH_2O \cdot CH_2CH_2CN)_3$ | 50,55 | 50,32 | +0,23 | 13,65 | 13,54 | +0,11 |
| | 50,49 | | +0,17 | 13,76 | | +0,22 |
| m-Nitroaniline $C_6H_6O_2N_2$ | 52,22 | 52,17 | +0,05 | 10,18 | 10,14 | +0,06 |
| | 52,19 | | +0,02 | 10,08 | | −0,04 |

*Nitrogen content calculated for the groups −CN and $-NH_2$.

It is of interest to note that determination of nitrogen in such compounds can be carried out in the presence of other forms of nitrogen ($-NO_2$, −NH−NH−, etc.). Examples of such determinations are given in Table 4.

Accordingly, in a number of cases, the wet combustion method can be used for the separate determination of various forms of nitrogen.

The method for the simultaneous determination of carbon, halogens, and nitrogen is also suitable for the analysis of compounds containing other elements. The combustion technique remains the same. When no halogens are present, flask 8 can be omitted.

Analysis of organic materials containing metals. During the oxidation of organic compounds containing metals, the latter, usually, remain in the reaction flask as the sulfates, since in this case complete mineralization occurs. The presence of chromic acid may lead to difficulties when metals are to be determined. Accordingly, when combustion is complete sexivalent chromium is reduced to the trivalent state by addition of a few drops of methanol. Complex compounds containing iron or copper were taken as test materials.

Iron was determined by treating the sulfuric acid solution with sodium sulfide, and, after removal of $H_2S$, the reduced iron was titrated with potassium dichromate in the presence of diphenylamine.

For the analysis of copper complexes, the copper was determined iodometrically in the sulfuric acid solution. This solution was then used subsequently for determination of nitrogen, the ammonia formed being distilled off in the usual way. Table 5 contains some examples of the analysis of complex compounds containing iron or copper.

TABLE 5

Simultaneous Determination of Carbon and Iron or of Carbon, Nitrogen, and Copper

| Test material | C, % | | | N, % | | | Metal, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | found | calc. | Difference | found | calc. | Difference | found | calc. | Difference |
| Iron isovalerylacetonate | 60,06 | 60,13 | −0,07 | | | | 11,45 | 11,65 | −0,20 |
| $C_{24}H_{39}O_6Fe$ | 60,00 | | −0,13 | | | | 11,35 | | −0,30 |
| Ferrocene $C_{10}H_{10}Fe$ | 64,77 | 64,56 | +0,21 | | | | 30,16 | 30,02 | +0,14 |
| | 64,73 | | +0,17 | | | | 29,93 | | −0,09 |
| Diacetylferrocene | 62,43 | 62,25 | +0,18 | | | | 20,56 | 20,68 | −0,12 |
| $C_{14}H_{14}O_2Fe$ | 62,42 | | +0,17 | | | | 20,77 | | +0,09 |
| Copper methylaminoacetylacetonate $C_{12}H_{20}O_2N_2Cu$ | 50,14 | 50,06 | +0,08 | 9,70 | 9,73 | −0,03 | 22,06 | 22,07 | −0,01 |
| | 50,24 | | +0,18 | 9,66 | | −0,07 | 22,29 | | +0,22 |
| Copper salicylalethylimine $C_{18}H_{20}O_2N_2Cu$ | 60,10 | 60,07 | +0,03 | 7,74 | 7,78 | −0,04 | 17,44 | 17,65 | −0,21 |
| | 60,35 | | +0,28 | 7,62 | | −0,16 | 17,54 | | −0,11 |
| Copper salicyalmethylimine $C_{16}H_{16}O_2N_2Cu$ | 57,79 | 57,91 | −0,12 | 8,47 | 8,44 | +0,03 | 19,04 | 19,15 | −0,11 |

TABLE 6

Simultaneous Determination of Carbon and Silicon

| Test material | C, % | | | Si, % | | |
|---|---|---|---|---|---|---|
| | found | calc. | Difference | found | calc. | Difference |
| Octaethylcyclotetrasiloxane | 47,08 | 47,00 | +0,08 | 27,43 | 27,48 | −0,05 |
| $C_{16}H_{40}O_4Si_4$ | 47,22 | | +0,22 | 27,69 | | +0,21 |
| Octamethylcyclotetrasiloxane $C_8H_{24}O_4Si_4$ | 32,17 | 32,39 | −0,22 | 38,03 | 37,88 | +0,15 |
| | 32,28 | | −0,11 | 37,94 | | +0,06 |
| Tetrabutylsilane* $C_{16}H_{36}Si$ | 75,03 | 74,91 | +0,12 | 10,73 | 10,95 | −0,22 |
| | 74,74 | | −0,17 | 10,85 | | −0,10 |

*In an atmosphere of pure oxygen, tetraethylsilane explodes when it comes into contact with the chromic mixture [7].

Analysis of organosilicon compounds. During the combustion of these compounds, silicon is oxidized completely and remains in the form of a gel of silicic acid. 2% gelatine solution was added for precipitating and speeding up the filtration of the silicic acid from the sulfuric acid solution. Filtration, calcination, and

weighing was carried out in porcelain crucibles with a porous bottom. When paper filters were used, considerable absorption of trivalent chromium salts was observed. In such cases it is necessary to wash the filter plus precipitate with hot hydrochloric acid (1 : 1).

Table 6 contains examples of the analysis of some organosilicon compounds.

Since most chlorine-containing organosilicon compounds are readily hydrolyzed, aliquots of such liquid materials were taken in glass ampoules. Obviously, such a method is inapplicable to the gravimetric determination of silicon. The following technique was adopted for taking aliquots of readily hydrolyzable materials. Into a tared beaker containing a small amount of anhydrous sodium sulfate was introduced a few drops of the test material under an atmosphere of dry nitrogen, the beaker was then gently tapped so that the salt covered the sample; the whole was then weighed again in a closed weighing bottle. The technique of covering the sample with sodium sulfate was also used for the analysis of solid hygroscopic materials, or for the analysis of materials which are decomposed by concentrated sulfuric acid with evolution of gaseous products (e.g. hydrochlorides). The sodium sulfate acts purely as a sealer. During the analysis the salt dissolves and does not interfere with the subsequent determination of silicon or other elements.

The following results were obtained during the simultaneous determination of carbon, chlorine, and silicon in chlorophenyltrichlorosilane:

| | | | | | | |
|---|---|---|---|---|---|---|
| $C_6H_4Cl_4Si$ | Found C, %: | 29.05; | Cl, %: | 57.38; | Si %: | 11.13 |
| | | 29.20; | | 58.46; | | 11.23 |
| | Calculated | 29.29; | | 57.65; | | 11.42 |

## SUMMARY

A "wet" method has been developed for the simultaneous determination of carbon, halogens, and nitrogen in organic materials. The sample is heated at 150-160° with a mixture of concentrated sulfuric acid and a concentrated aqueous solution of chromic acid. The oxidation products are carried by a current of oxygen through a heated (700-750°) tube containing a catalyst – chromic oxide on pumice. Carbon is thereupon oxidized to $CO_2$. The latter is absorbed with ascarite and weighed. Halogens are isolated in the elemental state or in the form of the hydrogen halides. They are absorbed by an acetic acid solution of hydrazine hydrate and are titrated argentometrically by the Volhard Method. Nitrogen is determined after combustion by the Kjeldahl method.

Iron, copper, silicon and other elements which are mineralized during the oxidation process, and remain in the sulfuric acid solution, can be simultaneously determined with carbon, halogen, and nitrogen.

## LITERATURE CITED

[1] J. Messinger, Ber. 21, 2910 (1888).

[2] A. A. Houghton, Analyst 70, 118 (1945).

[3] D. Van Slyke, Analyt. Chem. 26, 1706 (1954).

[4] W. P. Pickhardt, A. N. Oemler, and J. Mitchell, Analyt. Chem. 27, 1785 (1955).

[5] P. N. Fedoseev and M. M. Pavlenko, J. Anal. Chem. 8, 158 (1953);* P. N. Fedoseev and M. Ya. Sobko, J. Anal. Chem. 10, 323 (1955).*

[6] V. A. Klimova, M. O. Korshun, and E. G. Bereznitskaya, J. Anal. Chem. 11, 223 (1956);* V. A. Klimova and E. G. Bereznitskaya, J. Anal. Chem. 11, 292 (1956).*

[7] K. A. Andrianov, "Organosilicon Compounds", [in Russian], Goskhimizdat, Moscow, 1955, p. 100.

Received May 17, 1957

*Original Russian pagination. See C.B. Translation.

# NEW METHODS FOR THE QUANTITATIVE DETERMINATION OF HALOGENS IN ORGANIC MATERIALS. COMMUNICATION 4

P. N. Fedoseev and M. Ia. Sobko

The S. O. Makarov Nikolaev Shipbuilding Institute

Earlier we pointed out [1] that organic materials which contain nitrogen and sulfur in addition to halogens cannot be analyzed by the new gravimetric method, since the nitrogen and sulfur oxides formed during decomposition react with the halogens, and thereby distort the results. Later we established that under certain conditions the nitrogen oxides do not appreciably affect potassium and sodium bromides (at temperatures of 680-700°). This fact made it possible to extend the methods described earlier for the determination of halogen to materials containing chlorine, bromine, and nitrogen, or chlorine, iodine, and nitrogen.

The percentage content of chlorine in a material is determined from the change in weight of an absorption tube packed with sodium or potassium bromide, while the chlorine and iodine content is determined from the difference between total halogens trapped at the exit of the tube, and the chlorine content already determined.

Trapping of the halogens at the exit from the first absorption tube was accomplished by means of slightly moist crystalline sodium carbonate and a solution of alkali and perhydrol ($H_2O_2$). This makes it possible to carry out a separate quantitative determination of chlorine and bromine, and of chlorine and iodine in materials containing nitrogen, and also carry out a quantitative determination of halogens, one at a time, in materials containing nitrogen and sulfur.

Decomposition of halogen-containing organic materials on heating in a stream of oxygen is always accompanied by the formation of a considerable amount of a mist containing the halogens, which is difficult to trap. This makes it necessary to carry out an analysis at moderate temperatures, with a great deal of care; nevertheless, this often does not guarantee complete absorption of the reaction products. We managed to overcome this difficulty by using filter tubes filled with fine crystalline powders of halide salts [1], this made it possible to carry out the combustion at a faster rate and at higher oxygen throughputs. Under these conditions, the halogens are readily, rapidly, and completely trapped: the absorbed halogen can be determined quantitatively by one of the known methods.

Decomposition of an organic material is strongly facilitated in the presence of chromic oxide as a catalyst [2]. Chromic oxide is, however, an active catalyst, accordingly it must be used with caution. Thus, in the presence of this catalyst combustion of an aliquot of the test material weighing 0.0500-0.1000 g is complete in 2-3 minutes.

Excess oxygen is necessary for ensuring complete oxidation of the test material.

Chromic oxide in the form of fine, pressed lumps, in a layer 100-120 mm long, is placed at the end of the combustion tube (constant packing) and is heated to 850-900°. Oxidation of test material which is not burnt in the boat is completed on the catalyst.

Simultaneous, separate, quantitative determination of two halogens (chlorine and bromine, or chlorine and iodine) in organic materials containing nitrogen. The apparatus is assembled as shown in Fig. 1.

Combustion is carried out in a tube of transparent quartz 15-20 mm in diameter and 750-800 mm long; the tube contains lumps (2-3 mm) of pressed chromic oxide kept in position at both ends by small plugs of asbestos fiber.

The first oven is heated to 750-800°; it serves for evaporating and partially burning the test material. The second oven serves for heating (800-900°) the catalyst.

Tube c is heated to 680-700°, the temperature being measured with a thermocouple. The outlet in the absorption tube c is closed with glass wool.

The hygroscopic cloud from the absorption tube is removed by heating it to 600-700° in the stream of oxygen passed through at a rate of 200-250 ml per minute.

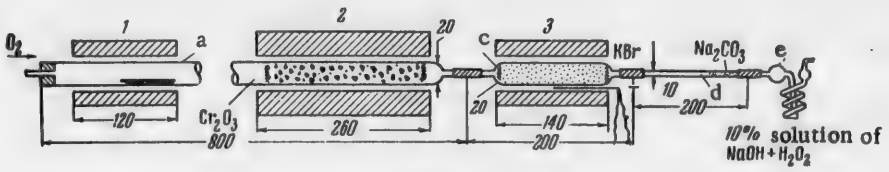



Fig. 1.

Tube d (200 mllong and 8-10 mm in diameter) is moistened with a 10% solution of alkali and perhydrol, excess of which is removed by slight shaking, after which one end of it is immersed in a supply of crystalline sodium carbonate, the tube being filled so as to give a layer 30-40 mm long.

3-5 ml of a 10% solution of alkali and 1.5-2 ml of perhydrol is introduced into the absorption apparatus e. The auxiliary apparatus is connected end to end to each other by means of rubber tubing 25-30 mm long. When the absorption tubes are properly packed, the oxygen should pass through freely at the rate of 200-250 ml/minute.

TABLE 1

| Test material | Chlorine, % | | | Bromine, % | | |
|---|---|---|---|---|---|---|
| | calc. | found | difference | calc. | found | difference |
| Polyvinylchloride<br>Nitrobromobenzene | 56,73 | 56,84 | +0,11 | 39,55 | 39,48 | —0,07 |
| Polyvinylchloride<br>Nitrobromobenzene | 56,73 | 56,71 | —0,02 | 39,55 | 39,61 | +0,06 |
| Dichlorobenzene<br>Nitrobromobenzene | 48,23 | 48,07 | —0,16 | 39,55 | 39,53 | —0,02 |
| Dichlorobenzene<br>Nitrobromobenzene | 48,23 | 48,06 | —0,17 | 39,55 | 39,32 | —0,23 |
| Hexachloroethane<br>Dibromobenzene<br>Nitrophenol | 89,85 | 89,66 | —0,19 | 67,75 | 67,68 | —0,07 |
| Hexachloroethane<br>Dibromobenzene<br>Nitrophenol | 89,85 | 89,90 | +0,05 | 67,75 | 67,46 | —0,29 |

Analytical procedure. Test material is weighed out in a porcelain boat and strewn with a thick quartz sand or $Cr_2O_3$.

Volatile liquids are taken in capillaries. The boat is moved inside the combustion tube to a distance of 2-3 cm from the beginning of the first oven. By gradually moving oven 1 forward the material is evaporated or ignited.

In order to ensure uniform combustion, marks are made on the side of the tube at the place where the boat is located, at 5 mm intervals. Oven 1 is left in the same position for 3-5 minutes from the inception of

combustion. Subsequently, at intervals of 30-60 seconds (depending on the character of the burning of the test material) the oven is moved forward.

Vapors of the test material plus its decomposition products are carried by the oxygen stream onto the heated zone where the catalyst is located; final decomposition takes place here.

During combustion, it is essential to keep the temperature of oven 3, in which the absorption tube c is located, constant.

When combustion is complete the oxygen is switched off. The contents of tube d and of apparatus e are quantitatively washed into the titration flask, while the absorption apparatus c is transferred to the balance room to cool. 3-4 ml of concentrated nitric acid is added to the titration flask and the whole boiled for 3-5 minutes. After cooling, 20 ml of 0.1 N silver nitrate is added to the contents of the flask, followed by 2-3 ml of ferric alum and excess silver nitrate back-titrated with potassium thiocyanate.

Since titrimetric determination is carried out more rapidly than gravimetric determination, we recommend working with two sets of absorption tubes.

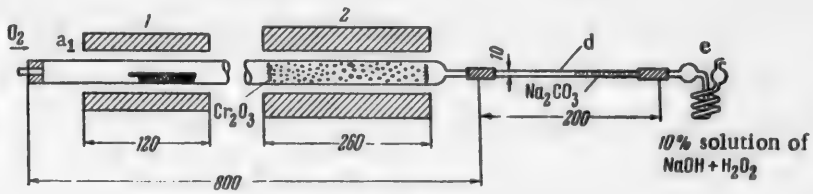



Fig. 2.

The second absorption apparatus d and apparatus e will contain the bromine from the sample and bromine liberated from the first absorption apparatus c; the amount of bromine in the sample will be equal to the total amount of bromine which has passed into the absorption tube d minus the amount of the bromine liberated by the chlorine from the first absorption tube c.

Results for the determination of chlorine and bromine are given in Table 1.

TABLE 2

| Test material | Halogen, % | | |
|---|---|---|---|
| | calc. | found | difference |
| Dichlorobenzene Thiourea | 48,23 | 47,98 | —0,25 |
| Dichlorobenzene Thiourea | 48,23 | 48,21 | —0,02 |
| Nitrobromobenzene Sulfosalicylic acid | 39,55 | 39,31 | —0,24 |
| Nitrobromobenzene Sulfosalicylic acid | 39,55 | 39,51 | —0,04 |
| Dichlorobenzene Nitrocinnamic acid | 48,23 | 48,18 | —0,05 |
| Dichlorobenzene Nitrocinnamic acid | 48,23 | 48,19 | —0,04 |
| Nitrobromobenzene | 39,55 | 39,45 | —0,10 |
| Nitrobromobenzene | 39,55 | 39,33 | —0,22 |
| Bromaniline | 46,45 | 46,20 | —0,25 |
| Bromaniline | 46,45 | 46,47 | +0,02 |
| Bromacetanilide | 37,33 | 37,16 | —0,17 |
| Bromacetanilide | 37,33 | 37,34 | +0,01 |
| Nitrochlorobenzene | 22,50 | 22,45 | —0,05 |
| Nitrochlorobenzene | 22,50 | 22,36 | —0,14 |

Materials containing chlorine and iodine. The iodine trapped in tube d and apparatus e can be determined quantitatively by one of the published methods, for example by the Leipert method [3].

Quantitative determination of halogens (chlorine, bromine, or iodine) in organic materials containing nitrogen and sulfur.

The analysis is carried out in the apparatus shown in Fig. 2.

The use of chromic oxide as a catalyst cuts down the time for an analysis to 20 minutes.

Absorption of halogens by means of moistened crystalline sodium carbonate and a solution of alkali and perhydrol makes it possible to determine halogens in the presence of nitrogen and sulfur.

The absorption tube d can be connected directly to the combustion tube. A lengthened layer (100-120 mm) of crystalline, slightly moist sodium carbonate serves both as a filter and as an absorber.

For titrimetric determination it is recommended that the test material in the boat be sprinkled with chromic oxide.

The rest of the analytical procedure is the same as that described above.

Chlorine or bromine are determined titrimetrically by the Volhard method.

Examples of some determinations are given in Table 2.

For the analysis of materials containing iodine, it is recommended that a gravimetric finish be used.

## DISCUSSION OF RESULTS

Existing techniques and methods for the quantitative, separate determination of several halogens on one aliquot of organic material possess a number of drawbacks. They take a long time to carry out, they are difficult, demand a number of operations, and the expenditure of expensive reagents (silver, platinum, etc.). The new method which we have developed makes it possible to carry out the separate, quantitative determination of two halogens (chlorine and bromine, or chlorine and iodine) in organic compounds containing nitrogen.

It has been established that under the experimental conditions we used, at a temperature of 600-700°, potassium (sodium) bromide does not react with nitrogen oxides, since the equilibrium recction $2NO_2 \rightleftharpoons 2NO + O_2$ is strongly shifted towards formation of the little-active nitric oxide under these conditions. On issuing from the heated absorption tube c, however, nitric oxide is readily oxidized to nitrogen peroxide which thereupon reacts with the damp potassium iodide. Accordingly, we replaced potassium iodide by crystalline sodium carbonate and a solution of alkali and perhydrol. We also used sodium bisulfate for this purpose as well as crystalline sodium carbonate; the results were promising. Other crystalline salts could probably be used for filling tube d. The filler in tube d plays the part of a filter for removing the mist formed and also as an absorbent for the halogens.

Before titrating with potassium thiocyanate, nitrogen oxides should be removed from the solution by boiling.

For a gravimetric finish during determination of chlorine, about 25-30 g of bromide is required for one filling of the heated absorption tube c. This amount of bromide is sufficient for more than fifty analyses for sample weights of 0.0500-0.1000 g. The success of an analysis depends to a very large extent on observance of a constant temperature in the absorption tube.

The methods described can be successfully used for analyzing organic compounds containing both mobile and immobile halogens. The method permits combustion of large aliquots, or of a series of aliquots, by passing the decomposition products through the same absorber; this means that it is possible to determine small amouts of halogen in test materials. The experimental error is ± 0.1-0.3%.

A gravimetric determination takes 50-60 minutes, while a titrimetric determination takes 20-30 minutes.

## SUMMARY

Chromic oxide has been used as a catalyst for facilitating combustion of test material. The mists formed during the decomposition of test halogen-containing materials, are destroyed by means of finely powdered

crystalline sodium carbonate or sodium bisulfate, with equal success to that obtained with the halogen salts tested previously.

It has been demonstrated that it is possible to carry out a simultaneous, separate determination of chlorine and bromine, or chlorine and iodine in organic materials containing nitrogen.

A method is described for the determination of chlorine, bromine, or iodine in organic materials containing nitrogen and sulfur.

## LITERATURE CITED

[1] P. N. Fedoseev and M. Ya. Sobko, J. Anal. Chem. 10, 323 (1955);* P. N. Fedoseev and M. Ya. Sobko, J. Anal. Chem. 13, 595 (1958);* P. N. Fedoseev and M. Ya. Sobko, J. Anal. Chem. 13, 701 (1958).*

[2] P. N. Fedoseev and M. M. Pavlenko, J. Anal. Chem. 5, 296 (1950); P. N. Fedoseev and M. M. Pavlenko, J. Anal. Chem. 6, 318 (1951); P. N. Fedoseev and M. M. Pavlenko, J. Anal. Chem. 8, 158 (1953);* P. N. Fedoseev, Chemistry in Schools, No. 1, 65 (1951); P. N. Fedoseev and R. M. Lagoshnaya, Chemistry in Schools, No. 4, 337 (1950); P. N. Fedoseev and R. M. Lagoshnaya, J. Anal. Chem. 9, 224 (1954);* P. N. Fedoseev and R. M. Lagoshnaya, J. Anal. Chem. 9, 37 (1954).*

[3] F. Leipert, Mikroch. Acta 3, 73 (1938).

Received June 22, 1956

*Original Russian pagination. See C.B. Translation.

RAPID METHODS OF MICROELEMENTAL ANALYSIS

# COMMUNICATION 16. THE RELATION BETWEEN THE LENGTH OF THE CONTACT LAYER AND THE METHOD OF DECOMPOSITION* DURING THE DIRECT DETERMINATION OF OXYGEN

M. O. Korshun** and E. A. Bondarevskaya

Institute of Elemental Organic Compounds Acad. Sci. USSR, Moscow

During the last fifteen years an important event in the development of microelemental analysis was the solution of the problem of the direct determination of oxygen. Published literature reviews illustrate how this problem, which was the object of an intense effort on the part of many chemists in the course of more than one hundred years [1-3], developed. The essence of the method generally accepted at the moment for the direct determination of oxygen is the thermal decomposition of the test material in a stream of pure nitrogen, the conversion of all the oxygen into CO over carbon which has been heated to 1100-1120° [4-6] or 1150° [2, 7, 9], and the subsequent oxidation of the CO into $CO_2$ which is then determined gravimetrically or titrimetrically.

Up to 1947 direct determination of oxygen was carried out only in Germany [4-6] and in the Soviet Union [2, 7, 9]. The method then widely entered into analytical laboratory practice in America [10-16] and Europe [17-22]. During recent years much work has been published on the direct determination of oxygen in various materials: in organic compounds [2, 4-7, 14, 19], coal [23-29]; in rubber, resin, gutta percha, petroleum products and asphalt [30-32, 11] and in inorganic materials [2, 4, 6, 33]. The method for the direct determination of oxygen has already found its place in the textbooks on quantitative organic microanalysis [9, 34-37].

Naturally, during such wide application, the method has been studied in detail by many analysts and many modifications and improvements have been made. Workers who have worked on improving the method have turned their attention to: 1) the preliminary purification of the inert gas used (nitrogen or helium) and to improvements in this technique [4-6, 9, 13, 14, 15, 21-22, 30]; 2) studying the sources of error connected with the quality of the quartz [14, 19-22, 34, 39-42]; the carbon [2, 4, 9-14, 18-19, 21, 43-47] and the iodine pentoxide [13, 38, 43-45, 48-51] used; and 3) to looking for a better way of determining the CO [11-12, 14, 19, 21-22, 27-28, 30, 46, 52-56]. Nevertheless, questions touching on the relation between the optimum value of the contact layer and the method of decomposing the test material have not yet been considered. The present article is devoted to this question.

From the experience gained in our laboratory on the determination of carbon and hydrogen, and the simultaneous determination of C and H and other elements, it has been established that preliminary pyrolysis of the test material facilitates quantitative oxidation [9, 57-61] as well as reduction [9, 62-63] of the aliquot considerably, as a result of which, it is not the vapors of the test material, but the active products of its decomposition, which are subjected to oxidation or reduction. Decomposition can be carried out in a similar manner during the determination of oxygen as well.

When the sample is placed in a quartz test tube and it is pyrolytically decomposed (i.e., the test tube is heated along the direction from the open end towards the closed end with an oven or with a burner) and the

*Communication 15, see J. Anal. Chem. 13, 695 (1958) [Original Russian pagination. See C.B. Translation.]

**Deceased.

material is not evaporated from the boat, as is usually done by all workers working on the direct determination of oxygen, then one might expect that the decomposition products issuing from the test tube will, undoubtedly, be much more reactive than the vapors of the undecomposed material, and will react considerably more easily than the latter with the contact layer of carbon at 1150°. Thanks to this a much shorter layer of carbon will be sufficient than that hitherto used. In order to convince ourselves of the efficiency of such a method of decomposition for the determination of oxgen, we carried out pyrolytic decomposition of the sample placed in a quartz test tube contained in an empty tube used for the decomposition, pure and dry nitrogen being passed through at the rate of 10-12 ml/minute. Since no carbon contact layer was present in the tube, the oxygen came off as water, carbon monoxide, and carbon dioxide. The carbon monoxide was oxidized to carbon

TABLE 1

| Test material | Weight of sample, mg | Oxygen found in the form of, % | | | Total oxygen found, % | |
|---|---|---|---|---|---|---|
| | | $H_2O$ | CO | $CO_2$ | absolute | relative |
| Saccharose | 5,509 | 30,98 | 7,86 | 7,31 | 46,15 | 89 |
| $C_{12}H_{22}O_{11}$, 51,42% O | 5,983 | 29,76 | 7,08 | 7,60 | 44,44 | 86 |
| Salicylic acid | 4,876 | 4,83 | 20,32 | 4,01 | 29,16 | 84 |
| $C_7H_6O_3$, 34,75 % O | 5,028 | 7,21 | 19,11 | 2,69 | 29,61 | 84 |
| γ-Methyl glucoside | 5,710 | 16,80 | 5,83 | 7,27 | 29,90 | 59 |
| $C_7H_{14}O_6$, 49,44 % O | 5,959 | 17,96 | 4,58 | 8,24 | 30,78 | 61 |
| Benzoic acid | 4,450 | 2,57 | 22,25 | 0,17 | 24,99 | 95 |
| $C_7H_6O_2$, 26 20 % O | 4,437 | 2,32 | 21,56 | 0,55 | 24,43 | 93 |
| Cis-4-ketocyclohexanedicarboxylic acid | 4,689 | 2,45 | 20,31 | 15,58 | 38,44 | 89 |
| $C_8H_{10}O_5$, 42,97 % O | 5,063 | 2,33 | 22,57 | 16,04 | 40,94 | 94 |

TABLE 2

| Test material | Wt. of sample, mg | % O | | Experimental conditions |
|---|---|---|---|---|
| | | found | difference | |
| Saccharose | 12,240 | 51,28 | −0,14 | Length of the contact layer of granulated carbon 5 cm, temperature 1150° Nitrogen throughput 10-12 ml/minute Decomposition of test material was carried out in a quartz test tube 7 cm long using a gas burner |
| $C_{12}H_{22}O_{11}$, 51,42 % O | 12,134 | 51,53 | +0,09 | |
| Salicylic acid | 13,745 | 34,56 | −0,19 | |
| $C_7H_6O_3$, 34,75 % O | 11,371 | 34,76 | +0,01 | |
| Cis-4-ketocyclohexanedicarboxylic acid | 4,025 | 42,87 | −0,16 | |
| $C_8H_{10}O_5$, 42,97 % O | 3,471 | 43,09 | +0,12 | |
| Dimethyl ester of azobenzoic--3,3'-dicarboxylic acid | 8,497 | 21,37 | −0,10 | |
| $C_{16}H_{14}O_4$, 21,47 % O | 8,486 | 21,42 | −0,05 | |
| Urea | 9,585 | 26,69 | +0,03 | |
| $CH_4ON_2$, 26,66 % O | 11,491 | 26,60 | −0,06 | |

dioxide over cupric oxide at 100° and the oxygen-containing products determined by weight. It was established in this way that during preliminary pyrolysis of an organic material carried out in a quartz test tube at 900-1000°, in an atmosphere of pure nitrogen, the tube used for decomposition being empty, the total percentage of oxygen calculated on the basis of the water and the carbon monoxide and dioxide amounts to 90% of the total content of oxygen in the test material (Table 1). Accordingly, when the method described above is used for decomposition, a considerable break down of the test organic material can be achieved. The fact that some of the oxygen is not accounted for can probably be ascribed to the presence of oxygen containing fragments of the molecule in the decomposition products.

Experiments were then carried out with a shortened layer of carbon in the decomposition tube. A layer of granulated carbon 5 cm long was placed in the quartz tube and heated to 1150° (± 20°) with a tubular oven 10 cm long. The aliquot was introduced into the tube in a quartz test tube 7 cm long; the latter was placed at a distance of 5-6 cm from the oven. The test tube was intially heated with a gas burner at the open end in the same way as for the determination of carbon and hydrogen [9, 57-63]. The gaseous decomposition products, on issuing from the test tube, were carried along with the nitrogen flow into the contact layer of granulated carbon heated to 1150°; here, all the oxygen contained in the vapor was quantitatively converted into carbon monoxide. The latter was oxidized to $CO_2$ by means of cupric oxide, the $CO_2$ being finally trapped with ascarite. The results obtained showed that the accuracy of the determination of oxygen in organic materials when the contact layer of carbon is shortened to 5 cm (Table 2) is adequate.

As our further experiments showed, determination of oxygen in organic compounds can also be carried out in an empty tube, when the contact layer of carbon is placed directly in the quartz test tube over the sample itself. A micro electric burner 6 cm long was used for heating the test tube at 1150°. By moving the burner slowly forward from the open end of the test tube towards the closed end, quantiative conversion of the oxygen in the sample to carbon monoxide was achieved in the test tube itself. The CO was subsequently oxidized as described above. Results of analyses carried out by this technique are given in Table 3.

TABLE 3

| Test material | Wt. of sample, mg | % O | | Experimental conditions |
|---|---|---|---|---|
| | | found | difference | |
| Saccharose | 6,601 | 51,25 | −0,17 | The contact layer of granulated carbon 5 cm long was placed in a quartz test tube 9 cm long. Decomposition was effected with a micro electric burner 6 cm long at 1150°. |
| $C_{12}H_{22}O_{11}$, 51,42 % O | 11,023 | 51,24 | −0,18 | |
| Benzoic acid | 6,930 | 26,17 | +0,03 | |
| $C_7H_6O_2$, 26,20 % O | 5,962 | 26,45 | +0,25 | |
| α, α, β-methyl ester of naphthalenetricarboxylic acid | 9,432 | 31,01 | −0,14 | |
| $C_{16}H_{20}O_6$, 31,15 % O | 8,593 | 31,00 | −0,15 | |
| 2, 2-Dimethyl-3-di-β-cyanethylpyrone | 8,397 | 13,49 | −0,18 | |
| $C_{13}H_{18}O_2N_2$, 13,67% O | 9,049 | 13,65 | −0,02 | |
| Uric acid | 7,905 | 28,62 | +0,05 | |
| $C_5H_4O_3N_4$, 28,57 % O | 7,481 | 28,72 | +0,15 | |

These experiments showed that by adopting preliminary pyrolysis of the test material in a quartz test tube, there is no need for a long contact layer of carbon. When the above technique is used, a carbon layer 5 cm long can be used instead of a 16-20 cm long layer. When this method is adopted, the carbon can be placed either in the decomposition tube or directly in the test tube containing the test sample. Accordingly, there is no need for a long tube for carrying out the decomposition, and it is possible to work with a tube which is only 30 cm long instead of 50 cm. Experiments which we have carried out in an empty tube, the carbon being placed inside the test tube used for decomposition, give a basis for hoping that in future it will be possible to cut down the length of the contact layer even more. The use of platinized carbon [63-65] made it possible for us to lower the temperature to 900°. A separate article will be devoted to this work.

## SUMMARY

It has been established that during the pyrolytic decomposition of material in a nitrogen atmosphere in a quartz test tube placed in an empty quartz tube, almost quantitative decomposition of the sample occurs, during which up to 90% of the oxygen is liberated as $H_2O$, CO, and $CO_2$.

Preliminary pyrolysis of the sample considerably facilitates quantitative formation of carbon monoxide, so that it is possible to cut down the length of the contact layer, and, accordingly, also cut down the length of the reaction tube.

It has been shown that it is possible to determine oxygen using an empty tube for decomposing the sample, the carbon layer being enclosed in the same quartz test tube as the sample itself.

## LITERATURE CITED


[1] Skanavi-Grigor'eva, Prog. Chem. 7, 713 (1938).

[2] M. O. Korshun, Dissertation Inst. Gen. Chem. USSR (1943); Trans. Commission on Anal. Chem. I (IV), 168 (1947).

[3] P. J. Elving and W. B. Ligett, Chem. Rev. 34, 1299 (1944).

[4] M. Schutze, Anal. Chem. 118, 244 (1939).

[5] W. Zimmerman, Z. Anal. Chem. 118, 258 (1939).

[6] J. Unterzaucher, Ber. 73B, 391 (1940).

[7] M. O. Korshun, Industrial Labs. 10, 241 (1941).

[8] M. O. Korshun and N. É. Gel'man. "Apparatus for Quantitative Elemental Micro Analysis", [in Russian] Moscow, 1947.*

[9] M. O. Korshun and N. É. Gel'man, "New Methods of Elemental Micro Analysis" [in Russian], Goskhimizdat, Moscow-Leningrad, 1949, p. 56.

[10] V. A. Aluise, R. T. Hall, F. C. Staats and W. W. Becker, Anal. Chem. 19, 347 (1947).

[11] R. A. Dinerstein and R. W. Klipp, Analyt. Chem. 21, 545 (1949).

[12] A. O. Maglott and J. B. Lewis, Analyt. Chem. 22, 1051 (1950).

[13] C. C. Harris, D. M. Smith, and J. Mitchele, Analyt. Chem. 22, 1297 (1950).

[14] V. A. Aluise, H. K. Alber, H. S. Conway, C. C. Harris, W. H. Jones, Anal. Chem. 23, 530 (1951).

[15] W. Kirsten, Anal. Chem. 25, 75 (1953).

[16] C. L. Ogg, Anal. Chem. 26, 116 (1954).

[17] C. E. Spooner, Bull. Soc. chim. France 26, 115 (1947); Metallurgia 37, 157 (1948).

[18] R. Berret and P. Poirier, Bull. Soc. chim. France 16, 539 (1949).

[19] R. A. Deinum and A. C. Schouten, Analyt. chim. acta 4, 286 (1950); 3, 353 (1949).

[20] R. Levy, Bull. Soc. chim. France 7/8, 672 (1952).

[21] A. Lacourt, Mikrochim. acta 735 (1954).

[22] A. F. Colcon, The Analyst 79, 784 (1955).

[23] E. A. Druyan-Rempel', and S. A. Babushkin, Industrial Labs. 16, 238 (1950).

[24] S. A. Babushkin and E. A. Druyan-Rempel', Industrial Labs. 17, 1418 (1951).

[25] E. A. Druyan-Rempel', Industrial Labs. 19, 430 (1953).

[26] S. G. Aronov, L. L. Nesterenko, and L. P. Sologub, Industrial Labs. 17, 1415 (1951).

[27] H. Guerin and M. Bastick, Bull. Soc. chim. France 3, 304 (1953).

[28] J. Garach and G. Weldener, Chim. Analyt. 36, 211 (1954).

[29] M. Bastick, Bull. Soc. chim. France 19, 308 (1952).

[30] W. W. Walton and W. H. Smith, J. Res. Nat. Bur. Standards 40, 493 (1947).

[31] P. Degens and J. Komnier, N. N. Maatschappij. Labor. Amsterdam Pepf. 11, 746 (1947).

[32] P. Gouverneuer, M. A. Schrenders and P. N. Degens. Analyt. chim. acta, 5, 293 (1951).

[33] O. Lourenco. Anais, Assoc. quim. Brasil. 10, 57 (1951).


*This reference seems to have been omitted in the original Russian – Publisher's note.

[34] F. Pregl-Roth, Quantitative organische Mikroanalyse 6, (1949) (Vienna) p. 73-84.

[35] A. Steyermark, Quantitative Organic Microanalysis. Philadelphia, 1951, p. 208.

[36] R. Belcher and A. L. Godbert, Semimicro Quantitative Organic Analysis.

[37] S. J. Clark, Quantitative Methods of Organic Microanalysis.

[38] J. Unterzaucher, Mikrochem. 36/37, 706 (1951).

[39] W. Kirsten, Mikrochem. 34, 151 (1949); 36/37,609 (1951).

[40] D. Lindqist, Acta chem. scand. 2, 177 (1948).

[41] R. Hey and H. J. Riley, Chem. Soc., London, 150, 1362 (1948).

[42] W. Otting, Mikrochem. 38, 551 (1951).

[43] J. Unterzaucher, Analyst 77, 584 (1952).

[44] J. Unterzaucher, Bull. Soc. chim France 32, 71 (1953).

[45] V. A. Companile, J. H. Badley, F. Brooks and E. Peters, Analyt. Chem. 23, 1421 (1951).

[46] J. Holowchak, G. F. C. Wear, Analyt. Chem. 23, 1404 (1951).

[47] M. Dandy and E. Stehr, Analyt. Chem. 23, 10, 1408 (1951).

[48] W. H. Jones, Analyt. Chem. 25, 1449 (1953).

[49] H. A. Pieters, Chem. weekbl. 43, 455 (1947).

[50] E. Huffman, Analyt. Chem. 23, 531 (1951).

[51] J. Unterzaucher, Mikrochim. Acta 4-6, 822 (1956).

[52] J. Unterzaucher, J. Chem. Ind. Tech. 22, 39 (1950).

[53] R. Hinkel and R. Raymond, Analyt. Chem. 25, 470 (1953).

[54] M. Schutze, B77, 484 (1944).

[55] D. Shepherd, Analyt. Chem. 19, 77 (1947).

[56] H. W. Deinum, Brenn. Chem. 35, 21/12, 334 (1954).

[57] M. O. Korshun and V. A. Klimova, J. Gen. Chem. 2, 274 (1947); 13, 476 (1948); 4, 292 (1949).*

[58] M. O. Korshun and N. S. Sheveleva, Proc. Acad. Sci. 60, 63 (1948); J. Anal. Chem. 7, 104 (1952);* 11, 376 (1956).*

[59] M. O. Korshun, J. Anal. Chem. 7, 96, 101 (1952).*

[60] M. O. Korshun, E. A. Terent'eva, and V. A. Klimova, J. Anal. Chem. 9, 275 (1952);* M. O. Korshun and E. A. Terent'eva, Proc. Acad. Sci. 100, 707 (1955).

[61] V. A. Klimova, M. O. Korshun, and E. A. Bereznitskaya, Proc. Acad. Sci. 84, 1175 (1952); 96, 81, 287 (1954); J. Anal. Chem. 11, 224 (1956);* V. A. Klimova and E. A. Bereznitskaya, J. Anal. Chem. 11, 292 (1956).

[62] N. É. Gel'man and M. O. Korshun, Proc. Acad. Sci. 72, 895 (1950); J. Anal. Chem. 12, 128 (1957).*

[63] M. O. Korshun and E. A. Bondarevskaya, Proc. Acad. Sci. 110 (1956).

[64] J. Oita and H. Conway, Analyt. Chem. 26, 600 (1954).

[65] F. H. Oliver, Analyst. 80, 593 (1956).

Received September 13, 1957

*Original Russian pagination. See C.B. Translation.

# QUANTITATIVE DETERMINATION OF THE THREE NITROCHLOROBENZENE ISOMERS IN THEIR MIXTURES BY MEANS OF THEIR INFRARED ABSORPTION SPECTRA

V. A. Pozdyshev and É. S. Levin

The K. E. Voroshilov State Scientific-Research Institute of Organic Intermediates and Dyes, Moscow

Analysis of mixtures of isomeric organic compounds, in particular, in the aromatic series of position isomers, is often a very difficult problem; as a result of the similarity of the properties of like isomers, the chemical, and also the most widely used physicochemical methods of analysis rarely achieve their ends. The most promising technique for aromatic isomers would appear to be the use of vibration spectra, in particular, infrared absorption spectra. The spectra of isomers usually differ considerably from each other, and can be used for analytical purposes.

Technical nitrochlorobenzene, both as a primary nitration product, and the various fractions obtained during successive distillations and crystallizations, are mixtures of the ortho and para isomers in varying amounts together with a small amount of meta isomer.* The usual method used for analyzing these products is doubly approximate. The ratio of the o- and p-isomers is established from the setting point, while the presence of the m-isomers is disregarded. The latter is determined bromometrically after reduction of the nitro group. This method is an indirect method, since all the three isomers use up bromine (the o- and p-isomers 4, and the m-isomer 6 atoms). The present article contains a description of the direct determination of the m- and p-isomers by means of their infrared absorption spectra; the amount of the o-isomer is determined by difference.

The spectra of the materials under discussion have already been studied [1], but in a narrower frequency range (500-1200 $cm^{-1}$) and without any emphasis on their possible analytical application. Within the range just indicated our results are in good agreement with published data [1].

## EXPERIMENTAL

Apparatus. The infrared absorption spectra were obtained on an IKS-11 single-beam instrument, the amplifying-recording setup of which was modified considerably. While not differing essentially from the set-up described previously [2], it was better designed from the point of view of selecting the operating conditions.

The photorelay with a high ohmic output is the first branch of a new recording system, and was achieved by simple redesigning of the FÉOU-15, as described in [2]; this was carried out as follows: the FÉSS-10 photoelement in the second cascade of the FÉOU-15 was replaced by STsV-4 vacuum photoelements. By substituting the first input galvanometer (coil resistance 12 ohms, redamped operation, sensitivity of $0.53 \times 10^{-7}$ amps/mm/m) which is the most sensitive to noise, by a third (output) galvanometer (coil resistance 200 ohms, redamped operation, sensitivity of $1.42 \times 10^{-6}$ amps/mm/m) the noise level was cut down. By making similar changes the amplifying factor of the photorelay was reduced, the photorelay is given the role not of an amplifier, but of a convertor of the signal from the low-ohm circuit of the thermoelement ($R_{T.E.}$ = 11.07 ohms) into the high-ohmic circuit of the vacuum photoelements ($R_{T.E.}$ is equal to several hundred megohms).

*It is only by using very efficient distillation columns that it is possible to isolate a fraction containing an appreciable amount of the m-isomer.

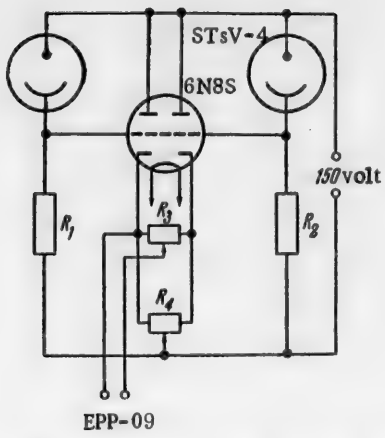



Fig. 1. Operating scheme of the cathodic repeater.

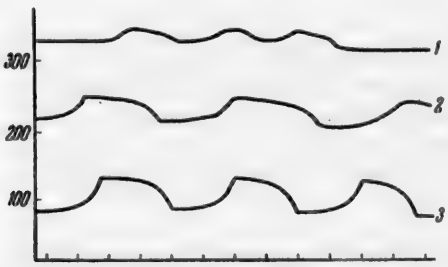



Fig. 2. An example of recordings of weak signals; 1) $1 \times 10^{-8}$ volt; 2) $2 \times 10^{-8}$ volt; 3) $3 \times 10^{-8}$ volt; (the whole scale of EPP-09 covers 15 millivolts).

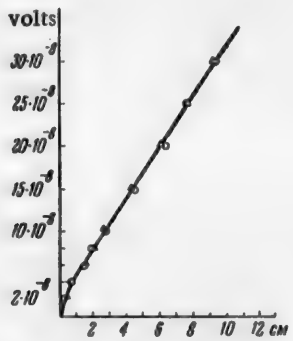



Fig. 3. Curve relating readings of the recording apapparatus (in cm) to the signal strength at the amplifier input (in volts).

It is known [3] that cathodic amplification can be relatively simply applied to signals in the high-frequency circuit of vacuum photoelements. It has been established [2] that a cathodic repeater is particularly suitable for this purpose [4].

The differential cathodic repeater (operating scheme) is shown in Fig. 1. The parameters of the dc current in the photometric setups are chosen with regard to the sensitivity and internal resistance of the recording apparatus. The latter was a EPP-09 electronic self-recording potentiometer, i.e. an apparatus with a low output resistance; thereby it was possible to get some freedom of choice for the loading resistance ($R_L$) in the cathodic repeater circuit. The cathodic resistance $R_C$ should be considerably greater than the load resistance for the greater slope of the amplifier. The basic parameters of the operating scheme of the cathodic repeater were as follows: $R_1 = R_2 = 22$ megohm, $R_3 = R_4 = 3$ kilohms , $R_C = 20$ kilohms. A double triode 6N8S with the parameters $\mu = 25$, $s = 4$ milliamp/volt was used (for a filament voltage of 6.3 volt and an anodic voltage of 240 volts).

The zero drift, in principle, is depressed largely due to the presence in the scheme of a strong negative back coupling (feedback) [4]. Low values of the supply voltage are also essential for zero stability. Special attention must be given to this point, otherwise it will be impossible to achieve satisfactory zero stability, even when stable supply sources are used such as NKN-45 accumulators, and BSG-70 high-frequency batteries on which our amplifier worked. Finally, it is important that the scheme should have the minimum number of control details. The choice of tubes and photoelements operating in the setup is not complicated; the only requirement is that the parameters in both halves of the triode should be equal to one another to within one percent, and that the sensitivities of the photoelements operating in pairs should be equal to within three percent; such a requirement is usual for elements of a balance scheme.

The operating conditions for the amplifying-recording system which were chosen experimentally were as follows: voltage of the filament of the tube of the photorelay lighting 1.6 volt; filament voltage of the electronic tube 5.9 volt; anode voltage and voltage on the SPV-4 photoelements = 150 volts. During the calibration of the scheme, the following indices were obtained: dark current of the photoelements $2.4 \times 10^{-10}$ amps; current $13 \times 10^{-8}$ amps; grid current of the tube $1 \times 10^{-9}$ amps; anode current 1.4 milliamp; sensitivity of the whole setup $2 \times 10^{-8}$ volt; amplification factor $2 \times 10^{4}$; zero drift 0.7 millivolt/hour; time constant about 10 seconds. In Fig. 1 are given examples of records of weak signals which give an idea of the sensitivity and the amplification factor of the new amplifying-recording system. An important property of the scheme is its good linearity at signals $\geq 4 \times 10^{-8}$ volt; this is illustrated in Fig. 3.

On the whole, the recording system which is characterized by maximum simplicity of preparation and control, ensures accurate and convenient recording of the spectra by means of a pen.

Automatic recording of spectra on the setup described above is completely satisfactory for the purposes of qualitative study of spectra, for identification of materials, etc. For the case of the quantitative analysis of mixtures, which is based on measurements of intensity, the small zero drift which occurs, as well as the insufficient constancy of the source of the infrared radiation, lead to an increase in experimental error. In this case, therefore, in order to measure the intensity of the "key" absorption bands we took readings on the basis of points as follows. First of all with the potentiometer covered from the radiation, a zero reading was taken; the radiation was then switched on, the solvent introduced into the beam and the "100% transmission" ($I_0$) reading taken. The zero reading was repeated and then the sample placed in the beam and the reading (I) taken. The transmission (in %) is given by the expression $T = I/I_0 \times 100$.

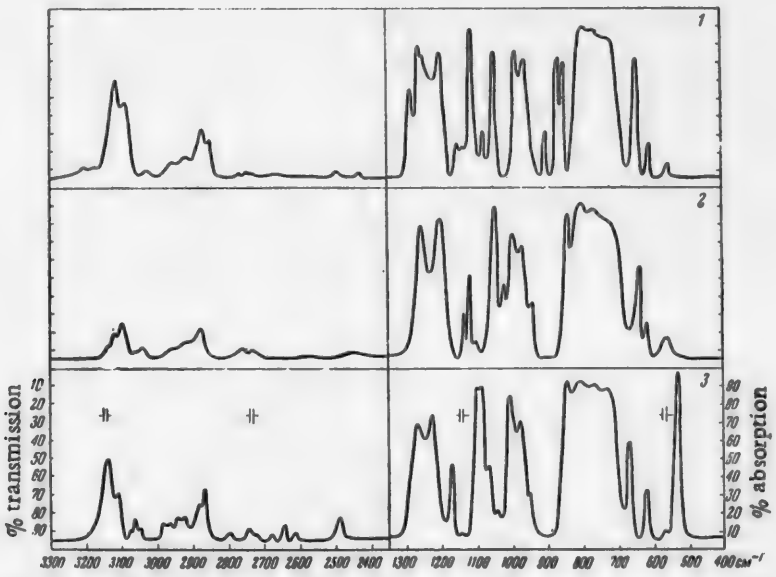



Fig. 4. Infrared absorption spectra of solutions of monochlorobenzene isomers: $l$ = 0.507 mm; 1) m-isomer (molar fraction 0.03070); 2) o-isomer (0.03058); 3) p-isomer (0.03079).

Test materials. The following materials were studied: m-nitrochlorobenzene, m.p. 43.5°; p-nitrochlorobenzene m.p. 33.9°; p-nitrochlorobenzene, m.p. 82.8°. These materials were prepared by purification (recrystallization) of industrial products. The solvent used was carbon tetrachloride, b.p. 75.0° (775 mm Hg); $n_D^{20}$ = 1.4620; this was obtained by washing, drying, and distilling the industrial product.

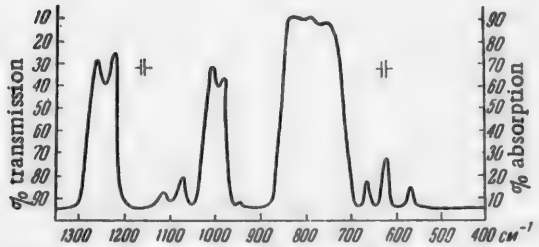



Fig. 5. Infrared spectrum of the solvent ($l$ = 0.507 mm).

Experimental results. The infrared absorption spectra of solutions of the nitrochlorobenzene isomers were taken over the ranges 100-1300, 2400-3300 $cm^{-1}$.* During the work in the spectral regions chosen, interchangeable prisms of potassium bromide, rock salt, and lithium fluoride were used. The spectral slit width in the 400-650 $cm^{-1}$ region, was about 11 $cm^{-1}$, in the 650-1300 $cm^{-1}$ region about 8 $cm^{-1}$, and at

*Absorption spectra in the 1300-2400 $cm^{-1}$ region were not studied for the reason that in this region there is considerable absorption by water vapor; this would have made it impossible, or, at least, very difficult to carry out analytical work without additional constructional modifications to the spectrometric setup.

3000-3300 $cm^{-1}$ it was equal to about 7 $cm^{-1}$.*

In Figs. 4 and 5 are given the spectra of the solutions and also of the solvent in the region where its selective absorption occurs (corrected for the scattered radiation of the high frequencies in the spectrometer).

The values of the frequencies which were measured with an accuracy of $\pm 3$, $\pm 5$ $cm^{-1}$ were as follows;

Meta-nitrochlorobenzene:: 3220, 3183, 3130, 3040, 2975, 2930, 2885, 2867, 2780, 2755, 2740, 2510, 2443, 1297, 1270, 1160, 1150, 1125, 1093, 1063, 917, 879, 867, 657 $cm^{-1}$;

Ortho-nitrochlorcbenzene: 3145, 3127, 3105, 3050, 2885, 2770, 2785, 1142, 1127, 1053, 1030, 950, 848, 647 $cm^{-1}$;

Para-nitrochlorobenzene: 3135, 3105, 3070, 3060, 3045, 2980, 2920, 2876, 2865, 2793, 2737, 2693, 2673, 2640, 2610, 2483, 1175, 1105, 1090, 1040, 1013, 953, 846, 675, 533 $cm^{-1}$;

Carbon tetrachloride: 1263, 1220, 1113, 1070, 1007, 980, 945, (700-800), 665, 623, 568 $cm^{-1}$.

The intensities of the absorption bands are not given since they can be obtained with the requisite accuracy (3% absolute) from the corresponding diagrams.

## DISCUSSION OF RESULTS

A complete interpretation of the vibrational spectra of such fairly complicated molecules as those of nitrochlorobenzene, is of considerable theoretical difficulty, and cannot be made on the basis of the infrared absorption spectra alone. For this purpose attention may be drawn to the data on combination scattering spectra and polarization measurements (see [6, 7] and the literature cited there). According to our experimental results (Fig. 4) it is possible to establish the characteristic spectral differences in the series of nitrochlorobenzene isomers. The infrared spectra of the m- and o-isomers are distinguished by narrow and strong absorption bands at 1063 $cm^{-1}$ and 1053 $cm^{-1}$ and such an intense band is absent in the spectrum of the p-isomer in this region; on the other hand, there is a very intense and very characteristic band with a frequency of 533 $cm^{-1}$. In turn there is a band with a frequency of 917 $cm^{-1}$ in the spectrum of the m-isomer. Despite the fact that this band is of low intensity, nevertheless, it can serve as a qualitative characteristic for the m-isomer, since the two other isomers do not generally have an absorption band in this region. The band at 879 $cm^{-1}$ is also very characteristic for the m-isomer.

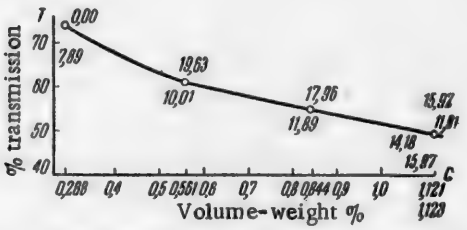



Fig. 6. Calibration curve for m-isomer: Figures on the left-concentration of p-isomer; figures on the right- concentration of o-isomer.

The observed spectral differences of the three isomers considered here are quite sufficient for recognizing them in their mixtures. The problem of quantitative analysis primarily reduces to looking for "key" absorption bands. Obviously there is no doubt that one can regard the band with a frequency of 533 $cm^{-1}$ for the p-isomer as a "key" band. It might also be possible to regard the band at 917 $cm^{-1}$ for the m-isomer as a "key" band, if it had a greater intensity. In addition to this band, another band in the spectrum of the m-isomer which attracts attention is the 879 $cm^{-1}$ band , although there is a danger that this band is not free from superposition from the bands at 848 and 846 $cm^{-1}$ of the o- and m-isomers, which are fairly close. By decreasing the spectral width of the slit** to 4 $cm^{-1}$ we were able to destroy completely the bands at 879 and 867 $cm^{-1}$ of the m-isomer, while a check on the superposition of the 879 $cm^{-1}$ band by the 848 and 846 $cm^{-1}$ band in this case, showed that for contents of 0.5-3% of the m-isomer in the mixtures, the experimental error in its determination did not exceed 10% (relative). When the m-isomer content of the mixture is greater than 5%,

*The spectral slit width was calculated by means of the formula generally accepted for infrared prism spectrometers, see [5].

**This decrease in slit width did not lower the accuracy of measurements of absorption band intensity in our setup.

the experimental error is only determined by errors in the measuring setup and amounts to (for measurements of of the intensity of the absorption bands on the basis of points) about 1% (relative). A detailed check established that the absorption band at 533 $cm^{-1}$ for the m-isomer is completely free from superposition by the bands of the other isomers.

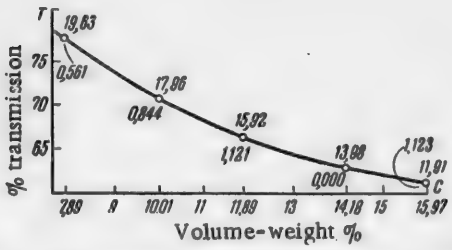



Fig. 7. Calibration curve for the p-isomer: Figures on the left — concentration of the m-isomer; figures on the right — concentration of o-isomer.

Thus, the bands at 879 and 533 $cm^{-1}$ can be regarded as "key" bands, and direct determination of the m- and p-isomers in their mixtures is possible by means of them. For this purpose calibration curves were constructed (Figs. 6 and 7), T = f(C), where C is the volume-weight concentration, T is the percentage transmission at 879 $cm^{-1}$ (or 533, respectively) in the spectrum; t is measured with an accuracy of 1%. The calibration curves shown in Figs. 6 and 7 were only obtained for mixtures of all three isomers in order to show graphically the insignificant superposition of the "key" absorption bands on other bands which are located close to them in the spectrum. For practical work it is sufficient to construct calibration curves for solutions containing just that isomer which it is desired to determine in a given mixture, since the experimental error has already been studied.

The percentage content of the isomers in a sample is calculated by means of the formula: % isomer = P·V/g, where P is the percentage of the isomer in solution, found from the calibration curve constructed on the basis of the measured transmission (T), V is the volume of the solution, and g is the weight of sample.

## SUMMARY

A method has been developed for the quantitative determination of the m- and p-isomers in technical nitrochlorobenzene. The lowest content determined is about 0.5%; the experimental error varies within ±1 and ±10% (relative).

## LITERATURE CITED

[1] J. Lecomte, J. Physique Radium VII, 9, 13 (1938).

[2] V. A. Pozdyshev, Yu. A. Pentin and V. M. Tatevskii, Bull. Moscow State University, No. 4, 221 (1957).

[3] A. M. Bonch-Bruevich, "The Use of Electronic Tubes in Experimental Physics", [in Russian], Gosteoretizdat, Moscow-Leningrad, 1950.

[4] "DC Tube Amplifiers", IL, Moscow, 1951.*

[5] R. Barnes, J. Appl. Phys. 16, 77 (1945).

[6] A. W. Reitz and W. Stockmair, Monatsh. Chem. 67, 92 (1935).

[7] H. Wittek, Z. Physik. Chemie 52, 315 (1942).

Received October 2, 1957

*Russian translation.

# BRIEF COMMUNICATIONS

## THE USE OF A "SOUNDING ARC" FOR INCREASING THE REPRODUCIBILITY OF QUANTITATIVE DETERMINATIONS IN SPECTROGRAPHIC ANALYSIS

Yu. I. Belyaev and E. E. Vainshtein

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

An essential drawback of a dc arc, which ensures comparatively high sensitivity during spectrographic determination, is the relatively low reproducibility and stability of the evaporation conditions of the elements, and of the excitation of their atoms. In order to increase the reproducibility of quantitative spectrographic determination of elements, and to increase the accuracy, use is made of a dc impulse arc [1]. Another possibility is, apparently, the use of a so-called "sounding" (Schalibogen) arc, which has already found use in radiotechnics [2] for obtaining undamped electromagnetic vibrations. The scheme of such an arc is shown in Fig. 1. The principle of its operation is as follows. It is known that the arc plasma which is included in the electrical circuit does not possess constant resistance. As a result of this the direction of the current on the electrodes changes continuously. When the arc is connected in an oscillating circuit (Fig. 1), the period of the characteristic vibrations of which is $T = 2\pi\sqrt{LC}$, then the vibration of the plasma will increase with this period, and in its turn will interact so as to increase the intensity of the vibration of the circuit. Under such conditions one should expect some stabilization of the arc discharge at a frequency $\omega = 1/T$, and an increase in stability of the working conditions of the arc following upon this. Outwardly, this is manifested by the arc beginning to sound when $\omega$ lies within the limits 50-20,000 cycles. In order to prevent the alternating component of the arc from shunting into the main circuit, and from being shunted by the current source, a large self-inductance $L_1$ is introduced into the circuit.

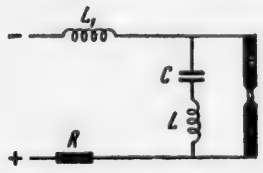



Fig. 1. Schematic diagram of a "sounding" arc.

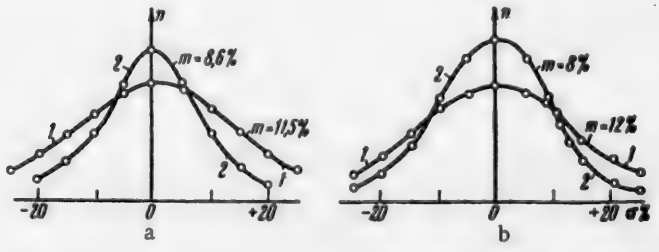



Fig. 2. Comparison of the curves for the distribution of errors during quantitative determination of hundredths of a percent of antimony (a), and whole percentages of gallium (b) in uranoso-uranic oxide by the Scribner-Mullin method [3]: 1) In the normal type of dc arc; 2) in a "sounding" arc.

An experimental check on the possibility of increasing the stability of the operating conditions of a dc arc by including it in the setup for a "sounding" arc gave encouraging results. As is evident from the curves

(Fig. 2), the distribution of errors in the case of excitation in a "sounding" arc, despite the rather crude way in which the experiments were carried out, is characterized by a smaller value for the standard error than when excitation is carried out in the normal type of dc arc.

More detailed information regarding the possibilities of a "sounding" arc in spectrographic analysis will be published later, after completing the investigation.

## SUMMARY

The use of a "sounding" dc arc is suggested for increasing the reproducibility of the spectrographic determination of elements.

## LITERATURE CITED

[1] E. E. Vainshtein and V. V. Korolev, J. Anal. Chem. 13, 627 (1958).*

[2] A. Eichenwald, Voresungen uber Elektrizität, Berlin, 1928, p. 528.

[3] B. Scribner and H. Mullin, J. Res. Nat. Bur. Stand. 37, 379 (1946).

Received June 6, 1958

*Original Russian pagination. See C.B. Translation.

# SPECTROGRAPHIC DETERMINATION OF BISMUTH, CADMIUM, TIN, LEAD AND ANTIMONY PRESENT AS IMPURITIES IN TANTALUM

E. I. Zakharov, L. V. Lipis, and K. I. Petrov

Production of high-purity tantalum has required the development of methods for determination of bismuth, cadmium, tin, lead, and antimony present as impurities in it. The permissible content of each of these impurities should not exceed $1 \times 10^{-4}$%. It is clear from this that any method of quantitative analysis used should possess a sensitivity of $3 \times 10^{-5}$%.

In order to overcome the difficulties arising during the spectrographic analysis of tantalum metal (the difficulty of preparing homogeneous standards from tantalum, possible liquefaction in the test sample, etc.), it is convenient to convert the metal into its oxide, the impurities being then determined in the latter.

In developing an analytical technique it was borne in mind that tantalum pentoxide is a relatively nonvolatile oxide, while the oxides of the five impurity metals to be determined are relatively volatile. This gave us grounds to hope that the evaporation method [1, 2] would be the most efficient method. In actual fact, the use of this method enabled us to achieve the necessary sensitivity for the determination of these five impurities in tantalum, the sensitivity in this case being higher than the sensitivity achieved by means of a dc arc [3].

The tantalum was oxidized by heating it in a muffle furnace at a temperature of 600-700° for 1.5-2 hours. The agreement between the results of spectrographic analysis of three samples of tantalum oxidized by two different methods: 1) by calcining the metal in a muffle furnace; 2) by dissolving the metal in a mixture of nitric and hydrofluoric acid, by repeated evaporation of the solution containing nitric acid, and finally calcining the precipitate to the oxide, indicates the absence or loss of impurities on calcining the metal to pentoxide in a muffle furnace at a temperature of 600-700° (Table 1).

In order to choose the temperature at which the samples of tantalum pentoxide can be heated so as to ensure complete or reproducible evaporation of the impurities, without evaporating the main component of the sample, the impurities were evaporated from 100 mg aliquots of the same sample at various temperatures starting at 900 and finishing at 1600°. The time for which the aliquots of the sample were heated was one minute. The experimental results indicated (Table 2) that the optimum temperature for heating the sample is 1400°. Using these conditions, the impurities studied evaporate completely, while the main component ($Ta_2O_5$) is hardly evaporated at all.

Copper was used as the material for preparing the electrodes on which the evaporated impurities were condensed. Spectrographically pure carbon can be used for this purpose, but the experimental accuracy in this case is almost halved. Distillation of the impurities from tantalum pentoxide was carried out in carbon crucibles.

The internal standard method was used for achieving reproducible results. The internal standard used was thallium which was added to test samples and standards in amounts of $1 \times 10^{-2}$%. The analytical pairs of lines used are given in Table 3.

The suitability of the analytical pairs of lines chosen for the determination was checked by changing the interelectrode gap, and the self-inductance of the spark generator.

The spectra of the impurities condensed on the electrodes were excited by means of a condensed spark discharge from a IG-2 generator (simple scheme, L = 0.15 microhenries, C = 0.01 microfarads).

The value chose for the analytical gap was 2 mm, since for this value the maximum blackening of the analytical lines was observed.

TABLE 1

Effect of the Method used for Oxidation on the Analytical Results

| Content of impurity, % | | | | | | | |
|---|---|---|---|---|---|---|---|
| Calcining in air | | | | Dissolution in acids | | | |
| Bi | Cd | Sn | Pb | Bi | Cd | Sn | Pb |
| $8,5 \cdot 10^{-5}$ | — | $2,0 \cdot 10^{-3}$ | $8,7 \cdot 10^{-4}$ | $8,0 \cdot 10^{-5}$ | — | $1,9 \cdot 10^{-3}$ | $9,0 \cdot 10^{-4}$ |
| $5,0 \cdot 10^{-5}$ | $4,2 \cdot 10^{-5}$ | — | — | $4,8 \cdot 10^{-5}$ | $4,4 \cdot 10^{-5}$ | — | — |
| $3,8 \cdot 10^{-5}$ | — | — | — | $4,0 \cdot 10^{-5}$ | — | — | — |

An ISP-22 quartz spectrograph was used for the work. The spectra were photographed on "spectrographic type III" plates. Exposure time was 10 seconds.

Tantalum pentoxide free from the impurity elements being determined was used for preparing standards. A check on the "purity" of the base material was carried out by the method of addition. The impurity elements were introduced in the form of solutions of their nitrates, while tantalum was introduced in the form of its sulfate. The mixture obtained was calcined for one hour at 500° and then ground up in a mortar. The remaining standards were prepared by diluting this stock standard with pure base material.

TABLE 2

Relation between the Blackening of the Analytical Lines of the Impurities and the Temperature at which the Tantalum Pentoxide is Heated*

| Temperature (°C) | Blackening | | | | |
|---|---|---|---|---|---|
| | Bi | Pb | Sn | Cd | Sb |
| 900 | 0,25 | — | — | 0,32 | — |
| 1000 | 1,28 | 0,21 | — | 1,33 | — |
| 1100 | 1,65 | 1,15 | — | 1,54 | — |
| 1200 | 1,82 | 1,68 | 0,34 | 1,85 | 0,36 |
| 1300 | 1,80 | 1,72 | 0,80 | 2,05 | 0,85 |
| 1400 | 1,92 | 1,92 | 1,36 | 2,00 | 1,49 |
| 1500 | 1,77 | 1,85 | 1,35 | 1,95 | 1,41 |
| 1600 | 1,80 | 1,95 | 1,32 | 2,00 | 1,42 |

*The analytical lines of the impurity elements given in Table 3 were used. The most intense lines for tantalum appear on the spectro grams when the samples are heated at 1500°.

TABLE 3

Analytical Pairs of Lines

| Element | Analytical line A | Excit. potential elec.volts | Reference line, A | Excit. potential elec.volts | Concentration range, % |
|---|---|---|---|---|---|
| Bi | 3067,72 | 4,0 | Tl 2918,32 | 5,2 | $1 \cdot 10^{-5}$—$1 \cdot 10^{-3}$ |
| Sn | 2839,99 | 4,8 | Tl 2918,32 | 5,2 | $3 \cdot 10^{-5}$—$1 \cdot 10^{-3}$ |
| Pb | 2833,07 | 4,4 | Tl 2918,32 | 5,2 | $3 \cdot 10^{-5}$—$1 \cdot 10^{-3}$ |
| Cd | 2833,02 | 5,4 | Tl 2580,14 | 4,8 | $1 \cdot 10^{-5}$—$1 \cdot 10^{-3}$ |
| Sb | 2598,53 | 6,0 | Tl 2580,14 | 4,8 | $1 \cdot 10^{-4}$—$3 \cdot 10^{-3}$ |

The sensitivity of the method is $1 \times 10^{-5}$% for Bi and Cd; $3 \times 10^{-5}$% for Pb and Sn; and $1 \times 10^{-4}$% for Sb.

The reproducibility of the method, which is characterized by the mean square error, is 8% for Bi; 10% for Pb and Sb; and 11% for Cd and Sn.

## SUMMARY

A method is described for determining Bi, Cd, Sn, Pb, and Sb present as impurities ($1 \times 10^{-4}$%) in tantalum; an evaporation technique is used after conversion of the tantalum into its pentoxide.

## LITERATURE CITED

[1] S. L. Mandel'shtam, N. N. Semenov, and Z. M. Turovtseva, J. Anal. Chem. 11, 9 (1956).*

[2] A. N. Zaidel', N. I. Kaliteevskii, L. V. Lipis, M. P. Chaika, and Yu. I. Belyaev, J. Anal. Chem. 11, 21, (1956).*

[3] Sh. G. Melamed and A. M. Saltykova, Industrial Labs. 13, 573 (1957).

Received September 18, 1957

*Original Russian pagination. See C.B. Translation.

# THE MASS-SPECTROMETRIC ANALYSIS OF THE ISOTOPIC COMPOSITION OF BORON

G. A. Semenov and Yu. A. Zonov

The A. A. Zhdanov Leningrad State University

The most widely used method for the determination of the isotopic composition of boron is the mass-spectrometric method in which boron trifluoride is used as the working material. During a study of the isotopic composition of boron in its oxide and acid, it is best not to convert the latter into $BF_3$, but to subject it directly to mass-spectrometric analysis. Shyuttse [1] studied the isotopic composition of boron in boron oxide, using an ionic source with a platinum crucible-evaporator and using $B^+$ ions; the accuracy was considerably lower than when $BF_3$ and $BCl_3$ are used, since it was not possible to get the required constancy for the source of the ionic currents. Inghram et al [2], while studying the mass spectrum of the vapors over liquid $B_2O_3$, detected $B_2O_3^+$, $B_2O_2^+$, $BO^+$ in the proportions 20 : 3.7 : 2.2 : 1.

Our measurements were made on the MS-1 and MS-4 mass spectrometers by the single-beam method. We were compelled to leave out the ionic source with the evaporating block which forms part of the MS-4 mass spectrometer, in view of the excessively large power used by the spiral of the source, which makes it difficult to control the current of the residual gases during the operation. We chose instead another ionic source, which in details of construction did not differ from that described earlier [3, 4] apart from the fact that the ribbon-evaporator was made from platinum on the surface of which was stamped out a cavity in the shape of a channel. The temperature of the ribbon was determined on the basis of the filament current, with preliminary calibration by means of an optical pyrometer. The optimum operating temperature of the evaporator was 1000-1200°.

About 0.5 mg of fused boron oxide was placed on the evaporator. This amount was sufficient for continuous work over a period of 3-4 hours, during which the stability of the ionic currents was completely satisfactory.

The following ions were observed in the mass spectrum of the vapors over boron oxide: $B_2O_3^+$, $B_2O_2^+$, $BO^+$ $B^+$ in the proportions of 19 : 3.1 : 2.2 : 1, which are in good agreement with published results [2]. Ions containing more than two atoms of boron were not detected. The isotopic composition of boron was determined using the ions $B_2O_3^+$ and $B^+$. Results of the study of $B_2O_3$ with a natural content of boron isotopes are given in Table 1.

The isotopic composition of boron in $B_2O_3$ was also determined by converting the latter into phenyldiazonium fluoroborate [5] with subsequent thermal decomposition of this material. The $BF_3$ liberated was analyzed on the mass spectrometer. These results are also given in Table 1. No corrections were applied for the content of the heavy isotopes of oxygen in making the calculations.

As is evident from Table 1, the results obtained during the measurements of the isotopic composition of boron on two different apparatus and at different times, are reproducible with reasonable accuracy.

Using the method developed, we determined the isotopic composition of boron for several samples of boron oxide with variable isotopic composition. Results of these experiments are given in Table 2. Here, as in the case of boron oxide $B_2O_3$ with a natural ratio of boron isotopes, we carried out a comparative determination, by converting the oxide into $BF_3$.

For removing the residues of test material completely, it is sufficient to wash the anode box, the ribbon-evaporator and holder, focussing block, and extension lens in alcohol.

TABLE 1

Isotopic Composition of Boron in $B_2O_3$ Without Enrichment with the $B^{10}$ Isotope

| Date on which meas. was made | Apparatus | Test material | Ion | Mean of 15-20 measurements |
|---|---|---|---|---|
| 06.VIII. 1957 | MS-4 | $B_2O_3$ | $B_2O_3^+$ | 4,16±0,05 |
| 08.VIII. 1957 | MS-4 | $B_2O_3$ | $B_2O_3^+$ | 4,18±0,04 |
| 12.VIII. 1957 | MS-4 | $B_2O_3$ | $B_2O_3^+$ | 4,15±0,04 |
| 14.VIII. 1957 | MS-1 | $B_2O_3$ | $B_2O_3^+$ | 4,15±0,01 |
| 16.VII. 1957 | MS-1 | $B_2O_3$ | $B_2O_3^+$ | 4,15±0,02 |
| 28.X. 1957 | MS-4 | $B_2O_3$ | $B_2O_3^+$ | 4,16±0,04 |
| 29.X. 1957 | MS-4 | $B_2O_3$ | $B_2O_3^+$ | 4,16±0,03 |
| 30.X. 1957 | MS-4 | $B_2O_3$ | $B_2O_3^+$ | 4,17±0,03 |
| | | | $B^+$ | 4,20±0,03 |
| | | | $B_2O_3^+$ | 4,17±0,03 |
| 21.XI. 1957 | MS-4 | $B_2O_3$ | $B^+$ | 4,18±0,01 |
| | | | $BF^+$ | 4,20±0,04 |
| 30.XI. 1957 | MS-1 | $BF_3$ | $B^+$ | 4,22±0,05 |

*Mean of 15-20 measurements.

Shyuttse [1] during the evaporation of $B_2O_3$ observed in two of the thirty experiments a change in the ratio of $B^{11}/B^{10}$ with time; this is contrary to what might be expected: at the beginning of the test there was observed preferential evaporation of molecules containing the heavy isotope $B^{11}$. The author does not give any theoretical foundation for this phenomenon. In our experiments the evaporation process took a comparatively short time, but orientating results indicated a normal process of isotope fractionation. All the same, insufficient experimental data do not give us the right at the moment to make any definite conclusion with regard to this effect.

TABLE 2

The Isotopic Composition of Boron in $B_2O_3$ Enriched with the $B^{10}$ Isotopic

| Sample No. | Test material | Ion | $B^{11}/B^{10}$ | Sample No. | Test material | Ion | $B^{11}/B^{10}$ |
|---|---|---|---|---|---|---|---|
| 1 | $B_2O_3$ | $B^+$ | 0,100±0,001 | 2 | $B_2O_3$ | $B^+$ | 0,112±0,003 |
| | | $B_2O_3^+$ | 0,098±0,002 | 3 | $B_2O_3$ | $B^+$ | 0,147±0,001 |
| 1 | $B_2O_3$ | $B^+$ | 0,100±0,001 | | | $B_2O_3^+$ | 0,145±0,003 |
| | | $B_2O_3^+$ | 0,097±0,001 | 1 | $BF_3$ | $B^+$ | 0,103±0,003 |
| 2 | $B_2O_3$ | $B^+$ | 0,108∓0,003 | | | | |

Taking into account the simplicity of the method suggested, and also the reasonable reproducibility and accuracy of the results, it can be recommended for the isotopic analysis of boron.


SUMMARY

A method of evaporation from a ribbon is used for the mass-spectrometric isotopic determination of boron in boron oxide and boric acid.

The isotopic composition of boron in boron oxide with natural and altered ratios of the isotopes has been measured.

The analytical results were checked by carrying out measurements with $BF_3$ as the working substance.


LITERATURE CITED


[1] V. Shyuttse, J. Exp. and Theor. Phys. 9, 486 (1955).

[2] M. G. Inghram, R. E. Porter and W. A. Chupka, J. chem. Phys., 25, 498 (1956).

[3] S. I. Zykov and N. I. Stupnikova, J. Anal. Chem. 12, 556 (1957).•

[4] L. E. Levina, Apparatus and Experimental Techniques No. 5, 114 (1957).

[5] G. M. Panchenkov and V. D. Moiseev, J. Phys. Chem. 30, 1119 (1956).

Received April 1, 1958

•Original Russian pagination. See C.B. Translation.

# DETERMINATION OF THE VARIOUS FORMS OF IRON IN ROCKS

Yu. P. Trusov

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry Acad. Sci. USSR, Moscow

Methods of determining iron in rocks have been extensively developed, and have been described in a number of textbooks [1-4]. Nevertheless, when we had to determine separately the various forms of iron in rocks (mainly in hydrothermally modified quartz porphyry), we were unable to find a published method which is rapid and fairly accurate. In the samples we had at our disposal, the iron (di- and trivalent-) was present partly in the form of oxides, partly combined as silicates, and also in the form of pyrites.

We adopted the following technique for determining di- and trivalent iron and iron combined in the form of pyrites, on one aliquot. 1 g (or 0.5 g) of rock which is not too finely ground is decomposed in a stream of $CO_2$ with a mixture of about 20 ml of dilute (1 : 2) sulfuric and about 10 ml hydrofluoric acid, in a special platinum test tube or crucible with an ebonite cover; through the latter a tube is passed which almost reaches the bottom. After cooling, the mixture is poured out into about 80 ml of a saturated boric acid solution and the ferrous iron determined by titration with 0.1 N potassium permanganate exactly according to the method described by Ponomarev [1], with the only difference that more boric acid is taken for complexing all the fluoride ions.

During the treatment described above, iron oxides and iron-containing silicates are decomposed, while the pyrites do not break down; grains of the latter are visible after titration under a magnifying glass. (For a discussion of the decomposition of pyrites when various methods are used for decomposing iron-containing materials, see Gillebrand et al [4], pp. 906 and 912).

Accordingly, after titration with permanganate, the solution is filtered through a loose filter and the precipitate washed with water until the washing give a negative reaction with thiocyanate (4-6 times) — a small amount of ammonium thiocyanate solution is placed in the funnel stem from which the wash liquors drop. To the filtrate, about 15 ml of 25% $NH_4SCN$ is added, and the total amount of iron contained in the sample and now brought into solution by the acid treatment as ferric iron, titrated with 0.1 N $Hg_2(NO_3)_2$ as described by Ponomarev [2]. The amount of $Fe^{III}$ is calculated by difference.

The filter paper plus pyrites is ignited and calcined at about 800° in a platinum or quartz crucible; the ferric oxide formed is fused with potassium pyrosulfate. The melt is dissolved on heating in dilute (1 : 20) $H_2SO_4$. A clear solution is obtained; occasionally a small crystalline precipitate is observed on the bottom of the beaker; this is, usually, insoluble sulfates. The solution is cooled (under the tap) and the iron originally contained in the pyrites, and now in the form of $Fe^{III}$ of solution, determined by titration with $Hg_2(NO_3)_2$.

The method is applicable to the analysis of materials not containing appreciable (in comparison with the iron content) amounts of oxidizing-reducing agents, i.e., to the analysis of most of the common rocks. The deviation between parallel determinations does not exceed more than some hundredths of a percent (absolute). The method gives good results for some tenths of a percent, and upwards, of iron in rocks.

Using this method, up to five determinations can be carried out in a working day, when one platinum test tube is available for decomposing the sample.

The basic virtue of the method is the possibility of carrying out a rapid and accurate determination of the various forms of iron on one aliquot; this excludes the error connected with the heterogeneity of the sample (especially since it is recommended that the sample should not be ground too fine so as to avoid oxidation); the method also permits determination when only a small amount of material is available.

The author wishes to thank P. N. Palei for valuable advice and help, and A. I. Ponomarev for acting as a consultant on the use of the mercurimetric method.

## SUMMARY

A method is described for the determination of di- and trivalent iron, and iron pyrite on one aliquot.

$Fe^{II}$ is determined by a permanganate titration after decomposition of the rock with HF and $H_2SO_4$. Pyrite is not decomposed by the acids and is filtered off; $Fe^{II} + Fe^{III}$ is then determined in the filtrate by means of $Hg_2(NO_3)_2$ titration. The pyrite is ignited and fused with $K_2S_2O_7$, and the iron titrated with $Hg_2(NO_3)_2$ after dissolving the melt.

The method can be used for the analysis of material not containing appreciable (in comparison with the iron content) amounts of oxidizing-reducing agents; i. e., it can be used for most of the usual rocks. The deviation between parallel determinations does not exceed some hundredths of a percent (absolute). The method permits determination of several tenths of a percent and upwards of iron in rocks.

## LITERATURE CITED

[1] A. I. Ponomarev, "Methods for the Chemical Analysis of Minerals and Rocks", [in Russian], Vol. I, Izd AN SSSR, Moscow, 1951.

[2] A. I. Ponomarev, Ibid, Vol. II.

[3] "Analysis of Mineral Raw Materials", [in Russian] Edited by Yu. N. Knipovich and Yu. V. Morachevskii, Goskhimizdat, Leningrad, 1956.

[4] W.F. Hillebrand, G. Lundell, H.A. Bright, and J. Hoffman, "Practical Textbook on Inorganic Analysis", [Translated from English], Goskhimizdat, Moscow. 1957.

Received September 15, 1957

# A MICRO METHOD FOR THE DETERMINATION OF FLUORINE MONOXIDE

E. A. Peregud and B. S. Boikina

State Scientific-Research Institute of Labor Hygiene and Occupational Diseases, Leningrad

Fluorine monoxide $F_2O$ is a colorless, extremely poisonous gas which is even more dangerous than elemental fluorine [1]. This makes it essential to carry out systematic control of the air in places where fluorine monoxide is used.

When present in high concentrations $F_2O$ is determined iodometrically [2]; $OF_2 + 4KI + H_2O \rightarrow 2I_2 + 2KOH + 2KF$.

The aim of the work described here was to develop a method for determining gamma amounts of $F_2O$ in air. Basing our efforts on the properties of $F_2O$ as a strong oxidizing agent, we tried to use analytical reactions of the oxidation-reduction type which are accompanied by the formation of a color directly in the absorptive solution. All the same, many experiments made along these lines did not yield satisfactory results. Fluorine monoxide, in contrast to elemental fluorine, reacts extremely slowly with aqueous solutions of reagents, which is explained, presumably, by its low solubility in water.

The essence of the method which we have developed for determination of traces of fluorine monoxide in air reduces to liberation of bromine from potassium bromide and formation of tetrabromofluorescein (eosin) which is colored red. On drawing air containing $F_2O$ through indicator powder on a silica gel base, the initial yellow color of the indicator changes to red; the length of the colored zone being proportional to the amount of fluorine monoxide. In the course of numerous experiments in which known amounts of $F_2O$ were used, the optimum conditions for determining the latter were established, and a conversion factor determined experimentally. Under the conditions we used, 1 mm of the colored zone was equivalent to 0.334 $\gamma$ $F_2O$.

Below is given the method for preparing the indicator tubes and the experimental procedure.

Glass tubes 45 mm long and with an internal diameter of 2.5 mm are filled with indicator powder.* A cotton wool plug is fitted into one of the glass tubes, while into the other end, the open end, is poured the indicator powder through a funnel with a drawn-out end; the indicator powder consists of silica gel Msk, 260-300 $\mu$, moistened with a solution of fluorescein containing KBr and $K_2CO_3$. By closing the upper end of the tube with the finger and lightly tapping the walls, the column of powder is packed, and sufficient powder introduced to give a column 40 mm long. The surface of the column is covered with a thin layer of cotton wool which is packed by squeezing it with the help of a fine metal rod. The ends of the tube are sealed with plugs and wrapped up in black paper for storage.

It is essential to standardize the conditions for preparing the indicator tubes, since the diameter of the tube, the packing density, the size of the silica gel particles, and the concentration of the reagents in the solution used for moistening the powder, all affect the length of the colored zone.

The fluorine monoxide content of the air to be tested is determined as follows: the plugs are removed from one of the tubes and one end connected to a 1 liter capacity aspirator; 1 liter of air is then drawn through at an uniform rate in the course of 20 minutes. The indicator tube is disconnected and the length of the red

*The method of preparing the indicator powder has been described in the article by Peregud and Boikina [3].

colored zone measured with a millimeter ruler. The fluorine monoxide concentration of the air is determined in γ/liter, using the coefficient 0.334.

## SUMMARY

A method for the determination of fluorine monoxide is based on liberation of bromine from potassium bromide and the subsequent formation of eosin. When air containing $F_2O$ is drawn through the indicator tube containing silica gel and fluorescein, the original color turns red. The length of the colored zone is proportional to the quantity of fluorine monoxide. Optimum conditions for determining $F_2O$ have been established.

## LITERATURE CITED

[1] "Fluorine and its Compounds", [Translated from English] Edited by J. Simons, Vol. I, II., Moscow, 1953, p. 73.

[2] Ibid, Vol. II, 1956, p. 54.

[3] E. A. Peregud and B. S. Boikina, J. Anal. Chem. 12, 513 (1957).*

Received February 16, 1957

*Original Russian pagination. See C.B. Translation.

# DETERMINATION OF THALLIUM BY HIGH-FREQUENCY TITRATION WITH SODIUM TETRAPHENYLBORON

A. R. Veis and A. F. Ievin'sh

Latvian State University, Riga

The solubility of thallium tetraphenylboron is 5-6 γ in 100 ml at 20° according to Geilmann[1]. We have studied the possibility of carrying out high-frequency titration (H. F. T.) of thallium with sodium tetraphenylboron:

$$Tl_2SO_4 + 2Na[B(C_6H_5)_4] = 2Tl[B(C_6H_5)_4] + Na_2SO_4.$$

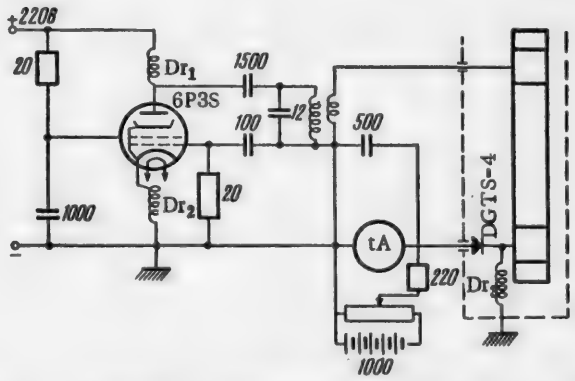



Fig. 1. Schematic diagram of the apparatus used for high-frequency titration.

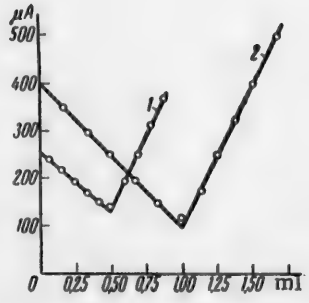



Fig. 2. Titration curves of thallium sulfate. 1) 1 ml of 0.1 N thallium sulfate; 2) 2ml of 0.1 N thallium sulfate.

Sander and Anke [2] have used sodium tetraphenylboron for the conductometric determination of potassium and ammonium. The advantages of H. F. T. have been pointed out in the work of Zarinskii and Mandel'berg [3].

Apparatus and experimental procedure. The setup used for the work was a modified form of the Blake apparatus [4] suggested by Resnais [5]; in this apparatus the strength of the high-frequency current passing through the titration cell is measured (Fig. 1).

The frequency of the high-frequency current used was about 14 megacycles; this permits work in solution down to 0.25 M concentration. A condenser-type cell with a capacity of 25-30 ml was used for titration. The high-frequency current passing through the cell was rectified with a germanium diode and was measured with a milliammeter.

The reagent was added from a semimicro buret and was read to an accuracy of ± 0.005 ml.

•Translated from the Russian.

The solution was agitated by means of a mechanical stirrer. The test solution of thallium sulfate was measured out with a pipet (or semimicro buret) and was diluted in the titration cell to 25 ml with water. The equivalence point was determined graphically by plotting the amount of solution added in ml along the abscissa, and the value of the high-frequency current, along the ordinate; when $R_{galvanometer}$ = 150 Ω, 100 divisions on the milliammeter corresponded to 0.5 ma. A titration curve is shown in Fig. 2. The lower the value of $R_{galvanometer}$ for a given sensitivity of the galvanometer, the higher the sensitivity of the apparatus at higher concentrations of the electrolyte.

Sodium tetraphenylboron was synthesized according to [6]. A 0.2 M solution was used; in order to remove insoluble impurities from the latter, 2 g of hydrated alumina was added per 100 ml of solution (bemite modification). The solution was agitated for one hour and then filtered. A solution prepared in this way and stored in a well sealed vessel, kept its titer for several months. It was standardized by H. F. T. against 0.1 N KCl.

Titration of Thallium with Sodium Tetraphenylboron

| 0,1 $N Tl_2SO_4$ ml | Impurity | Tl found, mg | Tl taken, mg | Error | |
|---|---|---|---|---|---|
| | | | | in mg | in % |
| 0,5 | — | 5,15 | 5,10 | +0,05 | 0,98 |
| 1,0 | — | 10,28 | 10,20 | +0,08 | 0,78 |
| 2,0 | — | 20,34 | 20,40 | −0,0 | 0,25 |
| 1,0 | 2 ml 0,1 *N* NaCl | 10,12 | 10,20 | −0,08 | 0,78 |
| 1,0 | 5 ml 0,1 *N* NaCl | 10,17 | 10,20 | −0,0 | 0,29 |
| 1,0 | 2 ml 0,1 *N* $ZnSO_4$ | 10,16 | 10,20 | −0,04 | 0,39 |
| 1,0 | 5 ml 0,1 *N* $ZnSO_4$ | 10,12 | 10,20 | −0,08 | 0,78 |
| 1,0 | 2 ml 0,1 *N* $CdCl_2$ | 10,19 | 10,20 | −0,01 | 0,09 |
| 1,0 | 5 ml 0,1 *N* $CdCl_2$ | 10,19 | 10,20 | −0,01 | 0,09 |
| 1,0 | 2 ml 0,1 *N* $Cu(NO_3)_2$ | 10,13 | 10,20 | −0,07 | 0,68 |
| 1,0 | 5 ml 0,1 *N* $Cu(NO_3)_2$ | 10,21 | 10,20 | +0,01 | 0,09 |
| 1,0 | 2 ml 0,1 *N* $CdCl_2$ + 2 ml 0,1 *N* $CuCl_2$ | 10,16 | 10,20 | −0,04 | 0,39 |
| 1,0 | 4 ml 0,1 *N* $ZnSO_4$ + 4 ml 0,1 *N* $CdCl_2$ + 2 ml 0,1 *N* $Cu(NO_3)_2$ | 10,19 | 10,20 | −0,01 | 0,09 |
| 1,0 | 2 ml 0,1 *N* $Na_2CO_3$ | 10,20 | 10,20 | — | — |
| 1,0 | 2 ml 0,1 *N* $H_2SO_4$ | 10,22 | 10,20 | +0,02 | 0,18 |
| 1,0 | 5 ml 0,1 *N* $CH_3COOH$ | 10,19 | 10,20 | −0,01 | 0,09 |

0.1 N thallium sulfate was prepared by weighing out the requisite amount of anhydrous $Tl_2SO_4$ (chemically pure grade).

The titration results obtained are given in the Table. As these results show, the presence of sodium, zinc, cadmium, and copper salts in solution does not interfere with the thallium deterimination.

## SUMMARY

A new method has been developed for the determination of thallium by high-frequency titration with sodium tetraphenylboron. Salts which do not react with sodium tetraphenylboron do not interfere with the determination of thallium. Thallium can be determined both in weakly acid and in alkaline media.

## LITERATURE CITED

[1] W. Geilmann, Ref. Angew. Chem. 66, 454 (1954).

[2] G. Sander and A. Anke, Z. analyt. Chem. 154, 9 (1957).

[3] A. V. Zarinskii and A. B. Mandel'berg, Industrial Labs. 22, 262 (1956).

[4] G. G. Blake, Australian J. Sci. 10, 80 (1947).

[5] A. Ya. Veis and Ya. Linaberg, Sci. Proc. Latvian State University, 14, 50 (1957).

[6] A. F. Ievin'sh and E. Yu. Gidrinietse, J. Anal. Chem. 11, 735 (1956). (See C.B. Translation).

Received September 30, 1957

## SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET CHEMICAL LITERATURE

| Abbreviation (Transliterated) | Significance |
|---|---|
| FIAN | Phys. Inst. Acad. Sci. USSR |
| GIPKh | State Institute of Applied Chemistry |
| GIREDMET | State Rare Metals Scientific Research Institute |
| GITI | State Sci.-Tech. Press |
| GITTL | State Tech. and Theor. Lit. Press |
| GLAVKhIM | Main Administration of the Chemical Industry |
| GOI | State Optical Institute |
| GONTI | State United Sci.-Tech. Press |
| Goskhimizdat | State Chem. Press |
| GOST | All-Union State Standard |
| Gostoptekhizdat | State Scientific and Technical Publishing house of the Petroleum and Mineral Fuel Industry |
| GTTI | State Tech. and Theor. Lit. Press |
| IFKhA | Institute of Physicochemical Analysis |
| IL | Foreign Lit. Press |
| IOKhAN | Institute of Organic Chemistry of the Academy of Sciences of the USSR |
| IONKh | Institute of General and Inorganic Chemistry (N. S. Kurnakov) |
| IONKhAN | Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR |
| INBI | Institute of Biochemistry |
| IREA | Institute of Chemical Reagents |
| ISN (Izd. Sov. Nauk) | Soviet Science Press |
| IVKhTI | Ivanovo Chemical Engineering Institute |
| Izd. AN SSSR | Acad. Sci. USSR Press |
| Izd. MGU | Moscow State Univ. Press |
| KEIN | Colloid Electrochemical Institute |
| Khimizdat | Chemistry Press |
| LGU | Leningrad State University |
| LIM | Leningrad Institute of Metals |
| Metallurgizdat | Metallurgy Press |
| MITKhT | Moscow Institute of Fine Chemical Technology |
| OIYaI | Joint Institute of Nuclear Studies |
| OKhN | Division of Chemical Science |
| ONTI | United Sci.-Tech. Press |
| OTI | Division of Technical Information |
| OTN | Division of Technical Science |
| RIAN | Radium Institute, Academy of Sciences of the USSR |
| RZhKhim | Chemical Abstract Journal (USSR) |
| VKhO | All-Union Chemical Society (Mendeleev) |
| ZhFKh | Journal of Physical Chemistry (USSR) |
| ZhRKhO | Journal of the Russian Chemical Society |

Note: Abbreviations not on this list and not explained in the translation have been transliterated no further information about their significance being available to us. — Publisher.